# PERTURBATIVE TREATMENT OF THE EXCHANGE INTERACTION IN THE PYROCHLORE LATTICE

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# Perturbative Treatment of the Exchange Interaction in the Pyrochlore Lattice

by

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# Contents

# Abstract

This thesis describes a theoretical investigation of magnetic systems based on corner-sharing tetrahedra in the pyrochlore lattice. $Er_2Ti_2O_7$ shows magnetic ordering at low temperatures. In order to understand the origin of this magnetic behavior, we have investigated the crystal structure and have found the possible ground states using group theoretical approaches. We investigate nearest neighbour exchange interactions on the pyrochlore lattice. The pyrochlore structure consists of vertex-sharing tetrahedra; there are two different types (A and B) of tetrahedra that differ by their orientation within the pyrochlore lattice. Each edge of each tetrahedron corresponds to a term in the exchange interaction. Our model assumes that the pyrochlore space group symmetry is broken such that exchange constants on the A tetrahedra are different than those on the B tetrahedra. The Hamiltonian describing exchange interactions on the A tetrahedra has an exact solution. We include the exchange interactions on the B tetrahedra using perturbation theory with periodic boundary conditions. Possible ground states for selected values of exchange interaction are calculated.

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# Prelude

And then there's the kind of thing which you don't understand. Meaning "I don't believe it, it's crazy, it's the kind of thing I won't accept." This kind, I hope you'll come along with me and you'll have to accept it because it's the way nature works. If you want to know the way nature works, we looked at it, carefully, that's the way it works. You don't like it, **go somewhere else! To another universe!** Where the rules are simpler, philosophically more pleasing, more psychologically easy. I can't help it! OK! If I'm going to tell you honestly what the world looks like to the human beings who have struggled as hard as they can to understand it, I can only tell you what it looks like. And I cannot make it any simpler, I'm not going to do this, I'm not going to simplify it, and I'm not going to fake it. I'm not going to tell you it's something like a ball bearing inside a spring, it isn't. So I'm going to tell you what it really is like, and if you don't like it, that's too bad.

**Richard P. Feynman**

Lecture at the University of Auckland

# Chapter 1

# An Introduction to Frustrated Spin Systems

## 1.1 Introduction

In the study of ordering phenomena, great efforts have been made to understand the basic mechanism responsible for the ordering and the nature of the associated phase transition. Understanding the underlying rules of a phase transition between different states is one of the main interests of theoretical physicists. A group of systems which have gathered a lot of interest recently are "frustrated spin systems", in which a spin in the system cannot find an orientation that satisfies all the interactions with surrounding spins. The interactions between spins are very complicated and will generally need rigorous calculations for an exact treatment of the problem. However, reasonable approximations can simplify the interactions to some well known models such as the Ising or Heisenberg models which are relatively easier to deal with. This simplification is discussed more in Section (2.3).

## 1.2 Frustration in Spin Systems

When systems consisting of spins, which are interacting with each other, are subjected to some constraints either from environment or the nature of their interactions, they might not be able to satisfy all these conditions. Frustration is the term used to convey this state of the system and as the meaning of the word frustration suggests, the system that is frustrated has a lot to do, or does not know what to do. It must satisfy two or more interactions which do not generally correspond to a simple definite classical state. Frustration in spin systems can have two different origins: competing interactions and lattice structure.

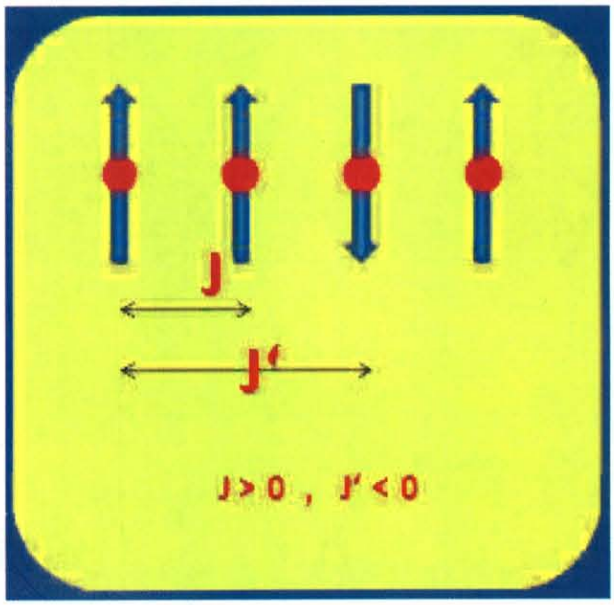


Figure 1.1: Competing interactions in a line of spin resulting in frustration. $J > 0$ is the exchange interaction constant between neighbouring spins and $J' < 0$ is the exchange interaction constant between next nearest neighbouring spins

In systems with different kinds of interactions, whether they are different in origin or magnitude, a spin may find it hard to satisfy all interactions with its neighbouring sites

completely and find a proper orientation. As can be seen in Figure 1.1, a ferromagnetic interaction ($J > 0$) between nearest neighbours (nn), and an anti-ferromagnetic interaction ($J < 0$) between next nearest neighbours (nnn), the ferromagnetic interaction between spins 2 and 3 cannot be satisfied if the anti-ferromagnetic interaction between spins 2 and 4 are satisfied.

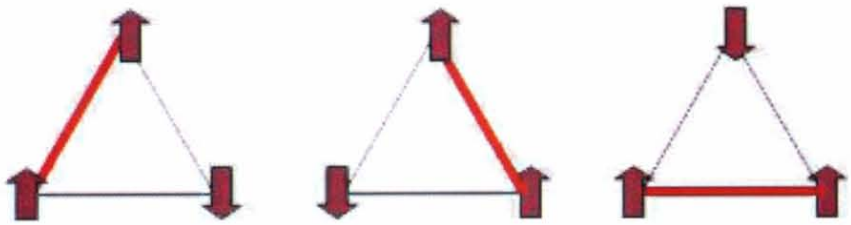

Figure 1.2: Lattice frustration in a triangular system. In each case, the red line shows the unsatisfied interaction.

Also, the connectivity or structure of the lattice might be such that it does not allow all of the interactions to be satisfied. Lattices such as triangular (see Figure 1.2), face-centred cubic (fcc), or hexagonal close-packed (hcp) with anti-ferromagnetic nearest neighbour interactions can result in frustration.

This kind of frustration which is due to the lattice structure is called "geometric frustration". Geometrically frustrated systems cannot minimize all of their bond interactions. However the ground state in which each plaquette has its energy minimized must also be a ground state for whole system [11]. The first experimental evidence for geometrical frustration in a ferromagnetic system goes back to 1997 [12].

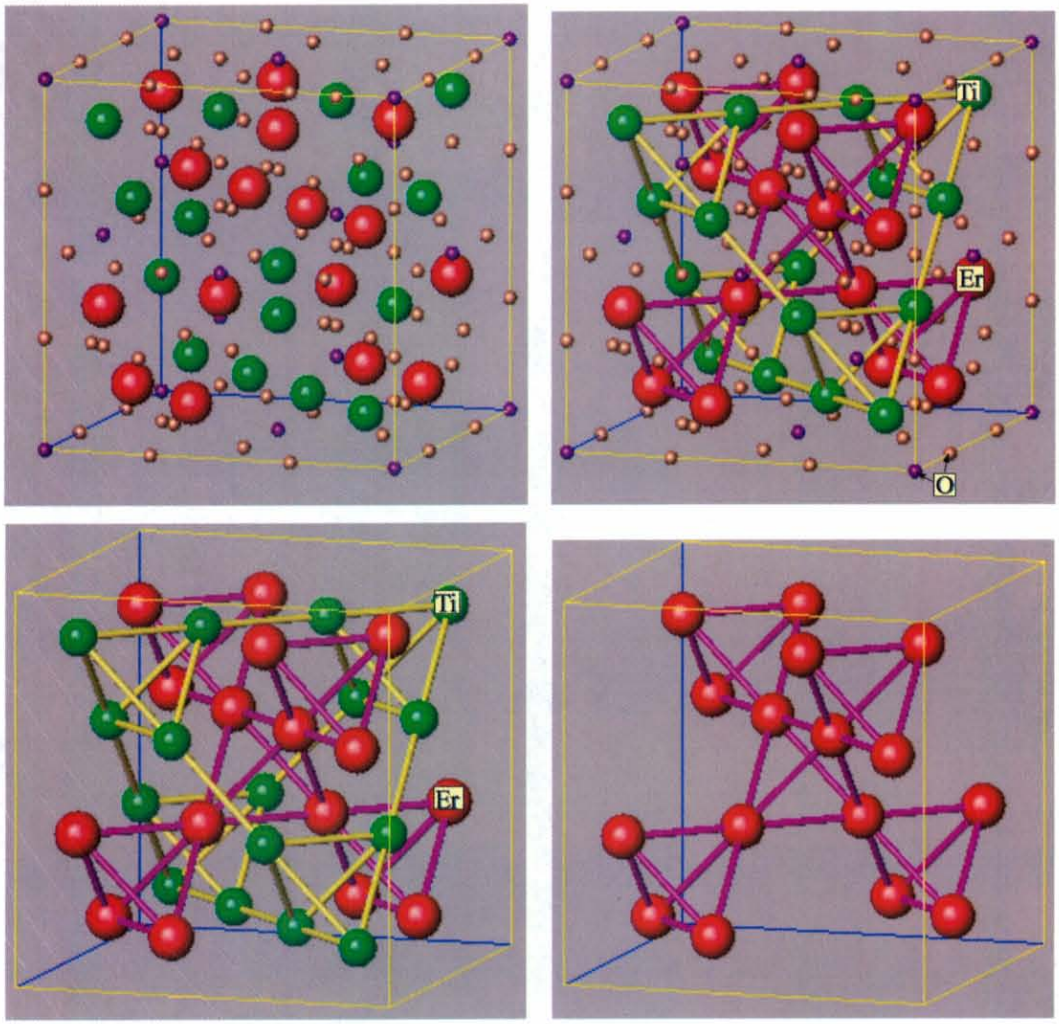


Figure 1.3: The fcc unit cell of $Er_2Ti_2O_7$. Top left shows all of the atoms, eight copies of chemical formula $Er_2Ti_2O_7$. Top right and bottom left show the tetrahedral networks of Ti and Er atoms.The bottom right shows the tetrahedral network of Er atoms only. The connections are exchange paths [23].

## 1.3 Physical Properties of $Er_2Ti_2O_7$

$Er_2Ti_2O_7$ was determined to be a cubic pyrochlore in 1965 [14] and has nearest neighbour anti-ferromagnetic interactions between Er atoms which make it is geometrically frustrated.

It belongs to the space group $Fd\bar{3}m$ ($\#227, O_h^7$) with fcc lattice translations (see Section (4.2)). There are two copies of the chemical formula per primitive unit cell and eight copies per face-centred cubic unit cell. Erbium and titanium both form tetrahedral networks. The magnetic properties are due to the erbium atoms which form a tetrahedral network shown in the bottom right of the Figure 1.3. The $Er^{+3}$ ion has a $4f^{11}$ configuration in a ${}^4I_{\frac{15}{2}}$ ($L$=6, $S$=$\frac{3}{2}$,$J$= $\frac{15}{2}$) state according to Hund's rules. The large value of $L$ suggests a significant amount of anisotropy in the system. The erbium spins show a magnetic ordering transition at $\sim$ 1.2 K [13] which does not have an explanation yet. A possible explanation is discussed in Section (5.3.2).

## 1.4 Tetrahedral Network

In $Er_2Ti_2O_7$, both erbium and titanium occupy the vertices of tetrahedral networks, however we are only concerned with the erbium network. The edges of the tetrahedra are nearest-neighbour exchange paths. The tetrahedra appear in two different orientations (as can be seen in Figure 1.3) that we call A and B which alternate in the network. Every A tetrahedron is connected to four B tetrahedra, and vice versa. The set of A tetrahedra are related to the set of B tetrahedra by some of the symmetry elements of the space group $Fd\bar{3}m$.

A single tetrahedron is a set of six exchange paths. The primitive unit cell contains twelve exchange paths that belong to one A tetrahedron and one B tetrahedron. The exchange interaction on the entire lattice can be conveniently divided into two parts, the sum over all A tetrahedra and the sum over all B tetrahedra. If one of these parts is neglected then the problem of the exchange interaction on the lattice is greatly simplified to the problem of the exchange interaction on a single tetrahedron, which has exact solutions. However, it implies that the space group symmetry is lowered via a lattice distortion [22].

The isolation of single tetrahedra is suggested by neutron scattering experiments, and

exact calculation of eigenstates of a single tetrahedron may help us to find the state of the network generally [22]. The reason why this can be true is still unresolved since because of the connectivity of this network, eigenstates of a single tetrahedron should not necessarily form eigenstates of the entire network. It was proposed by Curnoe [22] that a kind of lattice distortion, which lowers the point group symmetry but leaves the crystal system unchanged, can be applied to relieve geometrical frustration and arrive to an ordered state. This distortion does not remove the frustration symmetry but it will lead to isolation of single tetrahedra.

## 1.5 Crystal Electric Field

There are four Er ions in the primitive unit cell. Their local site symmetry (due to the electric field of the surrounding atoms in the crystal) is $D_{3d}$, where the 3-fold axes point along the different directions shown in Figure 1.4 [21]. The crystal electric field splits the 16-fold degeneracy of the $J = 15/2$ multiplet into singlets and doublets; the ground state is the doublet[26].

$$|\pm\rangle = \mp 0.475|\pm\frac{13}{2}\rangle - 0.418|\pm\frac{7}{2}\rangle \pm 0.572|\pm\frac{1}{2}\rangle \pm 0.241|\mp\frac{5}{2}\rangle \mp 0.463|\mp\frac{11}{2}\rangle \qquad (1.1)$$

where the quantization axis ($z$ axis) is along the 3-fold axis for each site. These states tend to lie in the plane perpendicular to the 3-fold axis, therefore it said that they have easy plane anisotropy [13].

In this thesis, in order account for the magnetic ordering which was experimentally observed in $Er_2Ti_2O_7$, we begin with exact solutions of a single A type tetrahedron, and add the effect of B type tetrahedra perturbatively. We consider two A type tetrahedra, perturbed by two B type tetrahedra with periodic boundary conditions and calculate the ground state of the system (see Chapter 5).

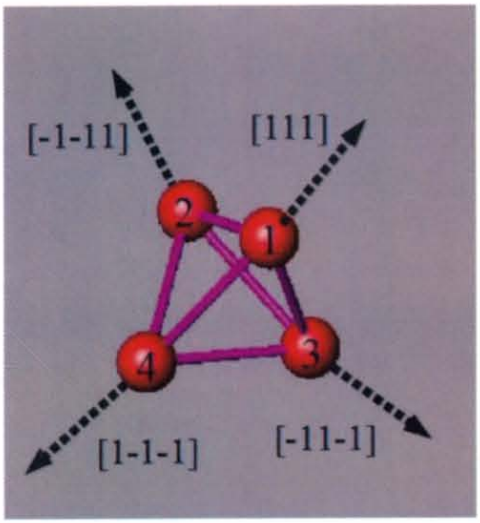


Figure 1.4: Local 3-fold (quantization or $z$ axis) sites on a tetrahedron [23].

In following Chapter, the quantum mechanical concepts, tools and methods used in this thesis are introduced. Chapter 3 introduces electron spin and its properties, as well as spin systems. An introduction to group theory and the space group $Fd\bar{3}m$ is the main subject of Chapter 4. In Chapter 5, we discuss the ground state for a single tetrahedron and we use perturbation theory in order to find the ground state of two tetrahedra. The final Chapter contains the conclusion and possible further works on the subject.

# Chapter 2

# Introductory Quantum Mechanics

## 2.1 Foundations of Quantum Mechanics

Quantum theory is the mathematical tool for describing how the physical world works in smaller scales. It may be, and it seems likely, that it does not have anything to do with the real underlying mechanism of physical phenomena, but above all the philosophical debates, it agrees with experiments. Feynman made a statement in one of his lectures which describes the quantum behavior of the nature versus the philosophy behind it. He said: *"A philosopher once said: It is necessary for the very existence of the science that the same conditions always produce the same results... Well, They don't"* [1]. For example, in the case of the double slit experiment, nature herself does not know which way the electron is going, even though it is prepared in the same way. Furthermore, as nature does not know herself, there is no way to resolve the problem more in order to find some hidden aspects inside an electron which can predict its exact trajectory. Any further resolution in the double slit experiment in order to track the electron down would destroy the interference pattern [1].

Quantum mechanics, like the other physical laws of nature, agrees with observation. However, it does not give us any mechanism of how nature actually works, just as some

other laws do not (such as gravity). Otherwise, nature should be a great mathematician to calculate her wave-function continuously in order to find her next move [1, 2].

Quantum mechanics can characterize the physical model by defining states, observables, measurements and dynamics [3]. States are the complete descriptions of the physical systems. They are considered as elements of the *Hilbert space* which is a complex vector space with a well defined norm and inner product. Observables are properties of physical systems that can be measured in principle. In quantum mechanics observables are self-adjoint operators which have real eigenvalues and orthogonal eigenstates. A measurement is the numerical outcome of an operation of the observable on the state of the system. Dynamics of the system, unlike classical dynamics, are governed by a linear equation (Schrödinger equation) [2, 3].

### 2.1.1 States

In classical mechanics, the state of a particle at any given time $t$ is specified by its position $x(t)$ and momentum $p(t)$ as a point in two dimensional phase space [4]. However in quantum mechanics states are elements of the Hilbert space $H$. A system made of single components can be described by the state $|\psi\rangle$. If a system is made of two components (bipartite), with one component living in $H_1$ and the other in $H_2$, then the system is known to live in $H = H_1 \otimes H_2$. This state is known as a tensor product state or a separable state, which admits the classical interpretation such that the first system is in state $|\psi_1\rangle$ and the second one is in $|\psi_2\rangle$. Such states have the general form of

$$|\psi\rangle = \sum_{i,j} C_{ij} |\psi_{i,1}\rangle \bigotimes |\psi_{j,2}\rangle \tag{2.1}$$

where 1 and 2 denote the system label, and $i, j$ are different states that these systems can have. The dimension of separable states is obviously $\dim H_1 + \dim H_2$. However the total space has a different dimension as the number of coefficient in $|\psi_{i,j}\rangle$ implies and is the product

$\dim H_1 \times \dim H_2$. The missing states are those which are not separable, that is, they cannot be factored as product of two separate states. They are known as entangled states [3]. The fact that the total dimension of the product states is much larger than just the addition of the dimension of just the two, in general, tells us that most of the states in a Hilbert space of a bipartite system are entangled which cannot have classical descriptions.

### 2.1.2 Observable

Observables are the properties of physical systems that can be determined by a series of observations, which have corresponding Hermitian operators which act on the Hilbert Space $H$. As their name suggests, observable values in principle could be verified as an outcome of experiment. In quantum mechanics, observables are Hermitian operators [2].

Observables and their definitions are sometimes considered as postulates in quantum mechanics (Born interpretation of quantum mechanics). To any self-consistent and well defined observable in physics, such as mass or energy or angular momentum, there corresponds a Hermitian operator **A** such that measurement of **A** will result in eigenvalues of A [5].

### 2.1.3 Measurement

Measurement in quantum mechanics has been a subject of debate between the founders and also the opponents of quantum theory. The measurement problem arises when you ask, "What was the state of the system just before the measurement?". The answer to this question leads to different interpretations of quantum theory. According to the Copenhagen interpretation of quantum mechanics, which is mainly accepted by theorists based on observation, measurement not only disturbs the system, but also produces the result. After the measurement, the wave function of the system is totally disturbed and has collapsed to a state which is the outcome of this measurement, and subsequently evolves according to the

Schrödinger equation.

### 2.1.4 Dynamics of the System

States are a complete description of physical systems. In classical mechanics, the state of a particle in any given time is a point in 6 dimensional phase space ($\vec{x}$ and $\vec{p}$ ), and the density matrix, which is an ensemble of different states with various probability evolutions is given by the *Liouville equation*. In quantum mechanics, the dynamics of a state is governed by the Schrödinger equation,

$$\imath\hbar\frac{\partial\psi(r,t)}{\partial t} = \widehat{H}\psi, \tag{2.2}$$

which is a linear equation. The $\widehat{H}$ on the right hand side is the Hamiltonian which is almost the same as the classical Hamiltonian with corresponding operators for each observable. Basically each Hamiltonian consists of different terms. Degrees of complexity in these terms determines the complexity of the problem. We can say our problem will reduce to finding solutions for the Schrödinger equation for different cases of $\widehat{H}$ which does not always have an exact solution.

## 2.2 Solution to the Schrödinger Equation

The Schrödinger equation (SE) plays a role analogous to Newton's second law in classical mechanics; having the initial condition $\psi(r,0)$, the SE determines $\psi(r,t)$ for all future times. However, finding eigenstates for a specific Hamiltonian is not an easy task generally. Once you have the eigenstates the rest is straightforward. But the main problem is solving an eigenvalue equation for given Hamiltonian. Most of the time, even for simple well-known cases like the harmonic oscillator potential, we use mathematical tricks in order to simplify the problem. The SE has been solved for a wide range of potentials [2, 4, 5]. However,

as in classical mechanics, the number of problems which can be solved exactly is small. In the majority of cases, we have to use some approximation in order to solve the problem. Different approximation methods are known and are widely used in tackling different problems: perturbation theory, the WKB approximation, the variational principle, the adiabatic approximation and the Born approximation are some of these methods. All of these methods are well discussed in most quantum mechanical textbooks. In this thesis, we solve the SE that uses the Hamiltonian known as Heisenberg-Dirac Hamiltonian, using perturbation theory.

## 2.3 The Heisenberg-Dirac Hamiltonian

If we want to include magnetic interactions in the Hamiltonian, we should consider that the dependence of the interaction energy of two or more magnetic moments on their relative directions is dominated by electrostatic interactions, rather than magnetic ones [6]. An estimate of magnetic dipolar interaction energies in electrons in solids typically 2 Å apart is no more than $10^{-4}$ eV [6]. A well-justified model of magnetic interactions applicable to insulators (and with considerable modifications to metals) which was developed for the case of a single hydrogen molecule, was also generalized to real solids. In the case of real crystal, the Heisenberg-Dirac Hamiltonian is a simpler mathematical model, than the original Hamiltonian, which consists of electron-electron interaction terms which cannot always be treated easily. The Heisenberg-Dirac Hamiltonian should lead to an energy spectrum that is similar to that of the original Hamiltonian (the SE with the relevant potential terms). If we assume that the crystal forms in a similar way as a hydrogen molecule, which consists of individual atoms containing one electron in the ground state, then the exchange Hamiltonian is equivalent to the original Hamiltonian. The Heisenberg-Dirac Hamiltonian was

constructed for such a two-electron system as follows:

$$H_{Spin} = -J\,\vec{S}_1 \cdot \vec{S}_2 \tag{2.3}$$

$$J = E_s - E_t \tag{2.4}$$

where $E_s$ stands for singlet energy and $E_t$ for triplet energy, where singlet and triplet are the possible spin configurations. Since $H_{Spin}$ is the scaler product of the vector spin operators, it depends on the relative orientation of spins and it will favour parallel spins if $J$ is positive and anti-parallel spins if $J$ is negative. It is clear that $J$ is positive or negative depending on which energy is lower, which is consistent with the fact that spins are parallel in triplet and anti-parallel in singlet [6]. In case of large number of ions, in many cases of interest, the form of Heisenberg-Dirac Hamiltonian can be generalized to all pairs of ions

$$H_{Spin} = -\sum J_{ij}\ \vec{S}_i \cdot \vec{S}_j \tag{2.5}$$

If the angular momentum of each ion contains an orbital as well as a spin part, then the coupling constant depends on the absolute as well as relative spin orientation and

$$H = -\sum J_{ij} \vec{J}_i \cdot \vec{J}_j, \tag{2.6}$$

where $\vec{J}$ is the total angular momentum. The exchange interaction is a purely quantum mechanical effect and it is the result of the wave function of indistinguishable particles being subjected to exchange symmetry and both bosons and fermions can experience it.

### 2.3.1 Solutions to the Heisenberg-Dirac Hamiltonian

Finding the ground state of the anti-ferromagnetic Heisenberg-Dirac Hamiltonian is an unsolved problem and only in one special case of a spin $\frac{1}{2}$ array in one dimension is the problem solvable analytically [6]. When we move on to more complicated geometries, it is almost impossible to have an analytic solution. Numerical methods like Monte Carlo simulations are

used in order to solve Heisenberg-Dirac Hamiltonian in different geometries and can be easily performed on a magnetic system. However, in this thesis, an analytical approach based on symmetry groups was taken in order to solve the Heisenberg-Dirac Hamiltonian in the specific case of the pyrochlore lattice with the aid of perturbation theory.

## 2.4 Perturbation Theory

### 2.4.1 General Formulation

Suppose that eigenfunctions of a Hamiltonian $H^0$ are known:

$$H^0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle. \tag{2.7}$$

Now we perturb $H^0$ by adding some term to it called $H'$,

$$H = H^0 + \lambda H'. \tag{2.8}$$

The factor $\lambda$ is to ensure that $H'$ is small enough so that it does not change the eigenstates of the system drastically, and mathematically makes it possible to expand the solutions in a power series. For large values of $\lambda$ perturbation theory does not necessarily hold, as the series might not converge. Perturbation theory is a systematic approach to obtain approximate solutions to the Schrödinger equation [2]. We rewrite our time independent (SE) for the general new Hamiltonian $H$:

$$H|\psi_n\rangle = E_n|\psi_n\rangle. \tag{2.9}$$

We write $|\psi_n\rangle$ and $|E_n\rangle$ as power series in $\lambda$:

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \lambda^2|\psi_n^2\rangle + \lambda^3|\psi_n^3\rangle + ... \tag{2.10}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \lambda^3 E_n^3 + ... \quad . \tag{2.11}$$

The method is very simple when the eigenvalue $E_n^0$ is non degenerate. We assume this for the remainder of this subsection. $E_n^1$ is the first order correction to the $n$th energy level, as $|\psi_n^1\rangle$ is the first order correction to the $n$th eigenstate. If we substitute $E_n$ and $|\psi_n\rangle$ by the the series above in (2.9), and also use equation (2.8) and then order by order in $\lambda$ we have

$$H^0|\psi_n^0\rangle + \lambda(H^0|\psi_n^1\rangle + H'|\psi_n^0\rangle) + \lambda^2(H^0|\psi_n^2\rangle + H'|\psi_n^1\rangle) + ... =$$
$$E_n^0|\psi_n^0\rangle + \lambda(E_n^0|\psi_n^1\rangle + E_n^1|\psi_n^0\rangle) + \lambda^2(E_n^0|\psi_n^2\rangle + E_n^1|\psi_n^1\rangle + E_n^2|\psi_n^0\rangle) + ... \quad . \tag{2.12}$$

The above equation is solved seprately for each power in $\lambda$ [7]:

$$(H^0 - E_n^0)|\psi_n^0\rangle = 0 \tag{2.13}$$

$$(H^0 - E_n^0)|\psi_n^1\rangle + (H' - E_n^1)|\psi_n^0\rangle = 0 \tag{2.14}$$

$$(H^0 - E_n^0)|\psi_n^2\rangle + (H' - E_n^1)|\psi_n^1\rangle - E_n^2|\psi_n^0\rangle = 0 \tag{2.15}$$

$$(H^0 - E_n^0)|\psi_n^m\rangle + (H' - E_n^1)|\psi_n^{m-1}\rangle \cdots - E_n^m|\psi_n^0\rangle = 0 \tag{2.16}$$

For the remainder of this chapter, the perturbative method is from *Quantum Mechanics* by Messiah [7]. We can select the phase so that $\langle\psi_n^0|\psi_n\rangle = \langle\psi_n^0|\psi_n^0\rangle = 1$. Using $\langle\psi_n|\psi_n\rangle = 1$ we obtain:

$$\langle\psi_n^0|\psi_n^1\rangle = \langle\psi_n^0|\psi_n^2\rangle = \cdots = \langle\psi_n^0|\psi_n^m\rangle = 0. \tag{2.17}$$

By considering the conditions in (2.17), Eq. (2.13) will give us the first order perturbed wave function and energy, while (2.14) will give us second order and (2.15) will give us $m$th order. One can use the Eq. (2.16) to extract $E_n^m$ by projecting on to the eigenfunctions of $H^0$:

$$E_n^m = \langle\psi_n^0|H'|\psi_n^{m-1}\rangle. \tag{2.18}$$

However, we have to obtain $|\psi_n^{m-1}\rangle$ in order to find this energy. Also, by projecting on to other basis vectors of $H^0$ we can find the corresponding component of $|\psi_n^m\rangle$ along each of them when $(E_l^0 \neq E_n^m)$:

$$\langle\psi_l^0|\psi_n^m\rangle = \frac{1}{E_l^0 - E_n^m}(\langle\psi_l^0|H' - E_n^1|\psi_n^{m-1}\rangle) - E_n^2\langle\psi_l^0|\psi_n^{m-2}\rangle - \cdots - E_n^{m-1}\langle\psi_l^0|\psi_n^1\rangle \tag{2.19}$$

Since $\langle\psi_n^0|\psi_n^m\rangle = 0$, $|\psi_n^m\rangle$ can be completely determined. We define an operator as follows:

$$Q_0 \equiv 1 - |\psi_n^0\rangle\langle\psi_n^0| = \sum_{E_l^0 \neq E_n^m} \sum_l |\psi_l^0\rangle\langle\psi_l^0| \tag{2.20}$$

and

$$\frac{Q_0}{a} \equiv Q_0 \frac{1}{E_l^0 - H^0} Q_0 = \sum_{E_n^0 \neq E_n^m} \frac{\sum_l |\psi_l^0\rangle\langle\psi_l^0|}{E_l^0 - E_n^0}. \tag{2.21}$$

With the aid of this notation, one can write $|\psi_n^m\rangle$ as follows:

$$|\psi_n^m\rangle = \frac{Q_0}{a}[(H' - E_n^1)|\psi_n^{m-1}\rangle - E_n^2|\psi_n^{m-2}\rangle - \cdots - E_n^{m-1}|\psi_n^1\rangle]. \tag{2.22}$$

In principle, we can use perturbation theory in order to find $m$th order correction to the state and also to the energy of the state. In short-hand notation [2], $V_{ln} \equiv \langle\psi_l^0|H'|\psi_n^0\rangle$, $\Delta_{ln} \equiv E_l^0 - E_n^0$ the first three corrections to $n$th energy level are

$$E_n^1 = V_{nn} \tag{2.23}$$

$$E_n^2 = \sum_{l \neq n} \frac{|V_{ln}|^2}{\Delta_{ln}} \tag{2.24}$$

$$E_n^3 = \sum_{l \neq n,k} \frac{V_{nk}V_{km}V_{nl}}{\Delta_{ln}\Delta_{nk}} - V_{nn}\sum_{l \neq n} \frac{|V_{ln}|^2}{\Delta_{ln}^2}. \tag{2.25}$$

### 2.4.2 Degenerate Perturbation Theory (DPT)

Depending on the symmetry of Hamiltonian $H^0$, it is possible that two or more of its eigenstates have the same energy. The addition of the perturbation Hamiltonian $H'$ might reduce the symmetry of the total $H$. In that case, the degeneracies maybe lifted due to the broken symmetry of $H$. Treating the degenerate states in perturbation needs more care than the non-degenerate states, since the denominator in (2.20) could be undefined in certain cases which can not lead to valid answer unless the numerator also vanishes. So we should seek another approach to the problem. In this case, even the first order correction to the energies determined by the formula of the previous section is not reliable any more.

If we consider the case of two eigenfunctions of $H^0$ with the same energy, it is clear that a linear combination of these states is also an eigenfunction:

$$H^0\psi^0 = E^0\psi^0 \tag{2.26}$$

$$\psi^0 = \alpha\psi_1^0 + \beta\psi_2^0. \tag{2.27}$$

To find the zeroth order correction to the energy and first order correction to the wave-function one find the matrix $W_{ij} \equiv \langle\psi_i^0|H'|\psi_j^0\rangle$ where $i, j = 1, 2$ and solve the eigenvalue equation

$$\begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_{1,2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{2.28}$$

to find the first order correction to energy and zeroth order correction to wave function. For a degeneracy of order $n$, one can extend the method above and build an $n \times n$ matrix $W_{n\times n}$ which will again yield the zeroth order correction to the wave-function and the first order corrections to the eigenvalue. For finding higher order corrections, one can take the following steps [7]:

1. The unperturbed Hamiltonian should be written in diagonal form. The representation of $H^0$ on the basis $|\psi_n^0\rangle$ has its eigenvalues along the diagonal.

2. We define the projection operator $\mathrm{P}_0$ which projects out the degenerate eigenfunctions (those we wish to apply the perturbation to),:

$$P_0 = \sum_{i=1}^{j} |\phi_{n_i}^0\rangle\langle\phi_{n_i}^0|, \tag{2.29}$$

   where $j$ is the degree of degeneracy corresponding to the subspace of $|\psi_n^0\rangle$. If $H^0$ is diagonal, then $P_0$ has 1's in the diagonal components and zeros everywhere else.

3. We find the matrix $\frac{Q_0}{a}$ defined by (2.21).

4. We have to write the matrix $H'$ using the same basis as the unperturbed diagonal Hamiltonian $H^0$.

5. We construct an operator called $K_\alpha$ which is a positive-definite Hermitian operator,

$$K_\alpha = P_0 - \lambda^2 P_0 H' \frac{Q_0}{a^2} H' P_0 + \cdots \tag{2.30}$$

and find its matrix representation.

6. We construct another operator called $H_\alpha$ which is also a Hermitian operator,

$$H_\alpha = E_n^0 K_\alpha + \lambda P_0 H' P_0 + \lambda^2 P_0 H' \frac{Q_0}{a} H' P_0 + \cdots \tag{2.31}$$

and find its matrix representation.

7. We solve the following equation which is a generalized eigenvalue equation,

$$H_\alpha |\psi_l^0\rangle = E_\alpha K_\alpha |\psi_l^0\rangle. \tag{2.32}$$

The eigenvalues $E_\alpha$ are the desired eigenenergies which are the solution of this secular equation:

$$\det(H_\alpha - x K_\alpha) = 0. \tag{2.33}$$

8. We find the projector operator:

$$P = P_0 + \lambda (P_0 H' \frac{Q_0}{a} + \frac{Q_0}{a} H' P_0) + \lambda^2 (\cdots) + \cdots \quad . \tag{2.34}$$

The projection of the corresponding eigenvectors $|\psi_l^0\rangle$ in (2.33) are the eigenvectors of $H'$.

In this thesis, these steps were followed in order to find the first order perturbed states and also shifts in energies as the result of a perturbation. A complete description of degenerate perturbation theory is given by Messiah [7].

In summary we discussed the basic quantum mechanical tools including degenerate perturbation theory. In Chapter 5, we will use these methods to solve the problem of finding spin states on the pyrochlore lattice with exchange interactions. In the following chapter, we introduce the concept of spin and basics of frustration in spin systems, as the investigated system $Er_2Ti_2O_7$ is a frustrated system.

# Chapter 3

# Spin and Spin Systems

**The universe is an enormous direct product of representations of symmetry groups.** *Steven Weinberg*

## 3.1 Electron Spin

Spin is a fundamental observable in quantum mechanics which lacks a classical analog. The first model of electron spin was a charged sphere rotating with fixed frequency and a radius given by

$$r_c = \frac{e^2}{4\pi\epsilon_0 m_e c^2} \tag{3.1}$$

Then it was shown that the velocity of the surface of the spinning electron should exceed the speed of light in order to produce the electron's angular momentum $\frac{\hbar}{2}$. The analogy with classical spin was abandoned, and the success of quantized angular momentum in explaining spin related phenomena led to its acceptance [8]. According to observation, if we prepare a spin in any manner and put it in magnetic field, it may emit a photon with a specific energy corresponding to the energy of flipping the magnetic moments 180 degrees, while a classical magnetic moment can emit a continuous spectrum of photons from 0 to 180 degrees. It

seems that if we measure the spin of an electron in any direction, it is either in that direction or opposing that direction and it is never something in between. It is either up or down, and we get a specific photon or we do not get anything. This picture of the electron makes it different from any classical counterpart. In three dimensional space, we use three operators which act on the spin state in order to measure the spin in $x$ or $y$ or $z$ direction. The quantum mechanical operator associated with spin observables are the Pauli spin matrices times a factor of $\frac{\hbar}{2}$:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3.2}$$

The eigenfunctions of $\sigma_z$ are:

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{3.3}$$

Suppose we measure the $z$ component of a spin and it turns out to be either up or down. What is the component of the same spin in $x$ or $y$ direction? In order to find the answer one should measure the desired direction of that spin. As mentioned in Section (2.1.3), measurement is an outcome of the observable which is a Hermitian operator which in this could be $\sigma_x$ or $\sigma_y$ or $\sigma_z$. This suggests that successive application of spin operators as it is in up $|+\rangle$ or down $|-\rangle$ eigenstates of $\sigma_z$ will result in:

$$\begin{aligned} \sigma_x|+\rangle &= |-\rangle \quad \sigma_x|-\rangle = |+\rangle \\ \sigma_y|+\rangle &= \imath|-\rangle \quad \sigma_y|-\rangle = -\imath|+\rangle \\ \sigma_z|+\rangle &= |+\rangle \quad \sigma_z|-\rangle = -|-\rangle \end{aligned} \tag{3.4}$$

## 3.2 Spin Systems

In a bipartite state as described in Section (2.1.1) one component can live in $H_1$ and another one in $H_2$, so the total state of the system can be found by taking the tensor product (direct product) of the two states. For example, if the first particle has spin $\frac{\hbar}{2}$ and the second has $-\frac{\hbar}{2}$, the tensor product is

$$|+\rangle \bigotimes |-\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \bigotimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = |+-\rangle \tag{3.5}$$

The spin observables can be constructed in a similar way, for example:

$$\sigma_x \bigotimes \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \bigotimes \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} \tag{3.6}$$

The operator (3.6) will measure the $x$ component of the first spin and $y$ component of the second spin. This method in principle can be used for $n$ electrons living in different Hilbert spaces. In this manner, measuring the spin on systems consisting of two or more spins would reduce to operating the product matrix on the product state.

### 3.2.1 Exactly Solved Model in Frustrated Systems

The first frustrated system which was studied was the triangular lattice with Ising spins and nn anti-ferromagnetic interactions [10]. If we consider an Ising-like interaction of the form

$$E = -J(\vec{S}_i \cdot \vec{S}_j) \tag{3.7}$$

where $J$ is the interaction constant that can be positive (ferromagnetic interaction) or negative (anti-ferromagnetic interaction). Obviously for a ferromagnetic system the minimum of energy is the configuration when all the spins are pointing in the same direction in any lattice system. However, this is not the case for anti-ferromagnetic interaction. In the $XY$ Heisenberg model, the ground state of the triangular lattice can be found by minimizing the energy of the a triangle. If we consider $S_i$ $(i = 1, 2, 3)$ to be the magnitude of spin on site $i$ and $\theta_i$ be the angle that it makes with positive $x$ direction, then the energy function would be

$$E = -J(\vec{S_1} \cdot \vec{S_2} + \vec{S_2} \cdot \vec{S_3} + \vec{S_3} \cdot \vec{S_1}) = JS^2(\cos(\theta_1 - \theta_2) + \cos(\theta_2 - \theta_3) + \cos(\theta_3 - \theta_1)) \quad (3.8)$$

where S=($S_x$,$S_y$). In order to find the minimum energy of the system, we should minimize the energy with respect to each variable of the energy function

$$\frac{\partial E}{\partial \theta_1} = \frac{\partial E}{\partial \theta_2} = \frac{\partial E}{\partial \theta_3} = 0. \quad (3.9)$$

By solving the coupled equation (3.9), one can find the the solution for a triangular lattice which is obvious even without further analysis ($\theta_1 - \theta_2 = \theta_2 - \theta_3 = \theta_3 - \theta_1 = 120°$)[9]. The same procedure could be used to solve the case of frustrated square plaquette with an anti-ferromagnetic bond. However, these are the rare cases that the model has an exact solution. Two frequently encountered frustrated spin systems with n.n. anti-ferromagnetic are fcc and hcp lattice which are formed by stacking tetrahedra with four triangular faces.

In summary, in this chapter, the basics of spin and spin systems and also spin frustration were introduced. In following chapter, basic of group theory is discussed as a mathematical tool which is used in applying these symmetry properties to the Hamiltonian and finding the eigenstates.

# Chapter 4

# Group Theory and the Spin State of a Single Tetrahedron

**To those who do not know mathematics it is difficult to get across a real feeling as to the beauty, the deepest beauty, of nature.** Richard P. Feynman

## 4.1 Point Groups and Space Groups

Group theory is a mathematical formalism developed to study symmetry. Physics laws are a mathematical interpretation of symmetries in nature. The symmetry of a crystal plays an important role in the study of different phenomena like the diffraction of light or the electronic and magnetic structure of crystal. The ideas of *point groups* and *space groups* provide us with tools which are used in studying those phenomena. In following sections, a brief summary and basic definitions needed to understand these tools are given.

A regular array of points in three dimensions which are mainly fixed in their places is the definition of a *lattice*, and if each of these points is occupied by a basis (which can be a molecule or a single atom) then we have a *crystal*. Since crystals do not extend to

infinity in all directions, we may impose periodic boundary conditions in order to conceal the effect of finite size. Symmetry transformations on crystal are classified in to two types: (i) translations and (ii) rotations, reflections and inversions. The latter type are known as *point group symmetries* due to the fact that they leave at least one point fixed in space while operating on the system. If point group symmetries accompanied by the translations, then they together constitute the *space group symmetries*. Crystals possesses space group symmetries while molecules possess only point group symmetries (except in the case of very long polymer chains). There are 32 distinct point groups and 230 distinct space groups.

### 4.1.1 Translations

The space group of a crystal is the set of symmetry operations that leave the crystal lattice invariant. A crystal has the property of being unchanged by translations through certain distances in certain directions, as it has spatial periodicity. Translation vectors in a lattice can be written in a general form:

$$\tau(k,l,m) = k\vec{u_1} + l\vec{u_2} + m\vec{u_3} \tag{4.1}$$

where $(k,l,m)$ are integers and $\vec{u_1}$, $\vec{u_2}$ and $\vec{u_3}$ are the set smallest of linearly independent translations. Every symmetry operation of the crystal lattice is a combination of a translation $\tau$ and point group operation $P$. The *Seitz* operator $\{P \mid \tau\}$ will denote this combination as follows:

$$\{P \mid \tau\}r = Pr - \tau \tag{4.2}$$

where $r$ is the position vector of some point in the lattice.

The successive operation of two such elements will result in the following:

$$\{A \mid \tau_1\}\{B \mid \tau_2\}r = \{AB \mid B\tau_1 + \tau_2\}. \tag{4.3}$$

And the inverse of an element is given by:

$$\{A \mid \tau\}^{-1} = \{A^{-1} \mid -A^{-1}\tau\}. \tag{4.4}$$

Generally, translations do not commute with point group elements. Moreover, the translational symmetries of a crystal are completely determined by the fourteen types of *Bravais lattices* [15, 17]. We can consider a subgroup $T$ as the translational subgroup of the space group $G$. Elements of the group $T$ are the translation operators $\{E \mid \tau\}$ where $\tau$ are lattice translations given by (4.1) and $E$ is identity element. Clearly, all translations parallel to $\vec{u_1}$ form a subgroup $T_{\vec{u_1}}$ and similarly for the directions $\vec{u_2}$ and $\vec{u_3}$. Since elements of the subgroups $T_{\vec{u_1}}$, $T_{\vec{u_2}}$ and $T_{\vec{u_3}}$ commute (all translations commute), group T is Abelian and a direct product of the three subgroups:

$$T_{\vec{u_1}} \bigotimes T_{\vec{u_2}} \bigotimes T_{\vec{u_3}}. \tag{4.5}$$

If we assume that the crystal is infinite, then we have infinite number of translations. This inconvenience is solved by the Born-von Karman (periodic) boundary condition. We assume that crystal has $N_1$ primitive cells along $\vec{u_1}$ axis. Using Seitz operators we can express the Born-von Karman condition as follows:

$$\{E \mid N_1\vec{u_1}\} = \{E \mid 0\}. \tag{4.6}$$

By using periodic boundary conditions we limited the number of translations along the $\vec{u_1}$ axes to $N_{x1}$ and the same procedure can be used for the other two axis. The total number of elements in group $T$ is therefore $N = N_1N_2N_3$.

### 4.1.2 Group Representation

In order to introduce the concept of a representation of a group, we give an example of a simple useful group and will find its representations [18, 19]. The Schrödinger group is

defined as the set of symmetry operators which leave the Hamiltonian invariant. It follows that Hamiltonian commutes with all of the Schrödinger group operations $g$:

$$gHg^{-1} = H \Longrightarrow gH = Hg, \tag{4.7}$$

Then if $\psi$ is an eigenstate of $H$, so is $g\psi$ with the same eigenvalue $E$,

$$g(H\psi) = H(g\psi) = E(g\psi). \tag{4.8}$$

Now suppose that the eigenvalue $E$ of $H$ has an $N$-fold degeneracy,

$$H|\varphi_i\rangle = E|\varphi_i\rangle; \quad i = 1, 2, ..., N. \tag{4.9}$$

Then any other state found as the result of operating elements of the Schrödinger group on any $|\varphi_j\rangle$ must be the linear combination of $|\varphi_i\rangle$'s

$$g_k|\varphi_j\rangle = \sum_{i=1}^{N} c_{ij}|\varphi_i\rangle. \tag{4.10}$$

The coefficients $c_{ij}$ form an $N \times N$ matrix $G(g_k)$ which corresponds to the operation $g_k$ of the group $G$, so the above equation can be more compactly rewritten as:

$$g_k|\varphi_1\varphi_2...\varphi_n\rangle = G(g_k)|\varphi_1\varphi_2...\varphi_n\rangle. \tag{4.11}$$

The set of matrices $G(g_k)$ is called a representation of the group $G$ and the set of functions $|\varphi\rangle = |\varphi_1\varphi_2...\varphi_n\rangle$ is called the basis of the representation. For example, suppose that we have a non-degenerate basis $|\varphi\rangle$ and a doubly-degenerate basis $|\psi_{1,2}\rangle$ with representations $G_\varphi(g)$ and $G_\psi(g)$:

$$g|\varphi_1\rangle = G_\varphi(g)_{11}|\varphi_1\rangle, \tag{4.12}$$

$$g|\psi_1\psi_2\rangle = \begin{pmatrix} G_\psi(g)_{11} & G_\psi(g)_{12} \\ G_\psi(g)_{21} & G_\psi(g)_{22} \end{pmatrix} |\psi_1\psi_2\rangle. \tag{4.13}$$

If we combine the basis $|\varphi_1\rangle$ and $|\psi_1\psi_2\rangle$ into a three-dimensional basis $|\varphi_1\psi_1\psi_2\rangle = |1\rangle$, the corresponding matrix $G_1(g)$ can be written as:

$$G_1(g) = \begin{pmatrix} G_\varphi(g)_{11} & 0 & 0 \\ 0 & G_\psi(g)_{11} & G_\psi(g)_{12} \\ 0 & G_\psi(g)_{21} & G_\psi(g)_{22} \end{pmatrix}. \tag{4.14}$$

The matrix $G_1(g)$ has a block-diagonal form, where the blocks are square matrices of different sizes. Representations of this form are said to be reducible [16]. Group theory provides us with ways to reduce representations or tells us that such a task is impossible, in which case the representation is said to be irreducible. In general, the bases of irreducible representations are sets of degenerate eigenstates [16, 18].

The energies and wave functions of an electron in a crystal are solutions of the Schrödinger equation. The potential term in the equation is due to the periodic lattice. The full symmetry group of Hamiltonian is the space group to which the crystal belongs. The solution to the Schrödinger equation in a periodic lattice turns out to have the form of *Bloch* functions which are introduced in next section. In the simplest case, if the potential is neglected or approximated as zero, then the electrons are "free" and the solutions are

$$\phi_k(r) = \exp(i\vec{k} \cdot \vec{r}) \quad ; \qquad E(k) = \frac{\hbar^2 k^2}{2m} \tag{4.15}$$

According to Bloch's theorem in the case of a periodic potential, the eigenfunctions have definite translation properties determined by the wave vector $k$ and eigenfunctions at equivalent points in different unit cells are simply related by a phase factor.

### 4.1.3 Bloch's Theorem and Symmetry in the Reciprocal Lattice

Consider the eigenvalue equation:

$$H|\varphi(r)\rangle = E|\varphi(r)\rangle. \tag{4.16}$$

If the potential term in $H$ is in the form of $V(r) = V(\vec{r} + \vec{\tau})$, then Hamiltonian is invariant under the translation group, and the eigenfunctions $\phi(r)$ can be used to generate an irreducible representation of $T$. The operation of any element of $T$ on $\phi(r)$ is just a scalar which forms a representation of $T$ with $\phi(r)$ as the basis. The action of any translation $P_{k,l,m}$ on $\phi(r)$ is

$$P_{k,l,m}\phi(r) = c(k,l,m)\phi(r) \tag{4.17}$$

and by definition we also have

$$P_{k,l,m}\phi(r) = \phi(r + k\vec{u_1} + l\vec{u_2} + m\vec{u_3}) \tag{4.18}$$

where $\vec{u_1}$, $\vec{u_2}$ and $\vec{u_3}$ are primitive lattice translation vectors. For instance, operating $P_{1,0,0}$ on $\phi(r)$, $N_1$ times yields

$$P_{N_1,0,0}\phi(r) = c(N_1,0,0)\phi(r) = c(1,0,0)^{N_1}\phi(r) \tag{4.19}$$

and using the periodic boundary condition we obtain

$$c(1,0,0) = \exp(2\pi i\frac{m_1}{N_1}) \tag{4.20}$$

where $m_1$ is an integer. Therefore the general form of $c(k,l,m)$

$$c(k,l,m) = \exp(2\pi i(\frac{m_1 k}{N_1} + \frac{m_2 l}{N_2} + \frac{m_3 m}{N_3})) \tag{4.21}$$

The definition of fundamental translations in reciprocal lattice is

$$\vec{v_1} = \frac{2\pi}{V}(\vec{u_2} \times \vec{u_3}); \quad \vec{v_2} = \frac{2\pi}{V}(\vec{u_3} \times \vec{u_1}) \; ; \quad \vec{v_3} = \frac{2\pi}{V}(\vec{u_1} \times \vec{u_2}) \tag{4.22}$$

A general $\vec{k}$ vector of reciprocal lattice can be written as a linear combination of $\vec{v_1}$, $\vec{v_2}$ and $\vec{v_3}$

$$\vec{k} = (\frac{m_1}{N_1})\vec{v_1} + (\frac{m_2}{N_2})\vec{v_2} + (\frac{m_3}{N_3})\vec{v_3} \tag{4.23}$$

where $m$'s are integers. If coefficients $\frac{m_1}{N_1}$, $\frac{m_2}{N_2}$ and $\frac{m_3}{N_3}$ are integers then such vectors are called reciprocal lattice vectors which are denoted

$$\vec{G}(h,k,l) = h\vec{v_1} + k\vec{v_2} + l\vec{v_3} \tag{4.24}$$

The scaler product of a general $\vec{k}$ vector and a translation vectors $\vec{\tau}(k,m,l)$ is then

$$\vec{k}\cdot\vec{\tau}(k,m,l) = 2\pi(\frac{m_1 k}{N_1} + \frac{m_2 l}{N_2} + \frac{m_3 m}{N_3}) \tag{4.25}$$

and $c(k,l,m)$ can be written as

$$c(k,m,l) = \exp\left[i\vec{k}\cdot\vec{\tau}(k,m,l)\right] \tag{4.26}$$

As a special case if we replace $\vec{k}$ by $\vec{G}$ then

$$\vec{G}\cdot\vec{\tau}(k,m,l) = 2\pi(hk + kl + lm) = 2\pi \times integer \tag{4.27}$$

Therefore the eignfunctions $\phi(r)$ have the property of

$$\phi(\vec{r}+\vec{\tau}) = \exp\left[i(k\cdot\tau)\right]\phi(r) \tag{4.28}$$

which can be satisfied if and only if $\phi(r)$ has the form

$$\phi(r) = \exp\left[i\vec{k}\cdot\vec{r}\right]u_k(r) \tag{4.29}$$

where the function $u_k(r)$ is periodic function with the same periodicity of the lattice. Bloch's theorem simply states that in periodic potential, eigenfunctions has the form of (4.29).

The reciprocal lattice has the same point group symmetry as the direct lattice, although it may not have the same type of lattice, for example a bcc lattice in direct space corresponds to a fcc lattice in reciprocal space. If we chose a lattice point in three dimension in a given lattice, the volume containing points nearer, or the most equidistant, to the chosen lattice

point than to any other lattice point is known as *Wigner-Seitz* cell. In other words, it is the volume enclosed by the perpendicular bisectors of the vectors from the chosen lattice point to all its neighbours. This cell has a particular property among all unit cells which are possible to chose, which is that it inherits the full point symmetry group of the lattice. The Wigner-Seitz cell in reciprocal lattice is called the *Brillouin zone*. Because of the properties mentioned above, the so-called Brillouin zone is the convenient choice for the unit cell in reciprocal lattice in the study of electronic structure of crystals. For every point on the boundary of the Brillouin zone, there is at least one other point on the boundary which differs from the first by a reciprocal lattice vector. All such points on boundary must therefore be treated the same and are assigned the the same value of $\vec{k}$ [6, 15, 18].

The point group of the vector $\vec{k}$ (the little group) is defined as the set of symmetry operations that leave $\vec{k}$ invariant or transform it into an equivalent vector $\vec{k} + \vec{G}$. Irreducible representations of the little groups of are called *small representations*. Bloch functions corresponding to equivalent vectors transform under the same representation so such a basis is clearly reducible. The star of a arbitrary vector $\vec{k}$ [15], which is the set of destinct $K$ vectors obtained by applying all the symmetry to $k$, determines the irreducible basis for translation group when corresponding functions are symmetrized with respect to the small representations of the vector $\vec{k}$. Accordingly, each irreducible representation of the space group is defined by $k^*$ and the small representations.

## 4.2 Properties of the Space Group Fd$\bar{3}$m

As mentioned in chapter one, the space group symmetry of $Er_2Ti_2O_7$ is Fd$\bar{3}$m (# 227, $O_h$), with fcc lattice transition, and the point group is octahedral $O_h$.

O is the group of proper rotations which take a cube or an octahedron to itself (see

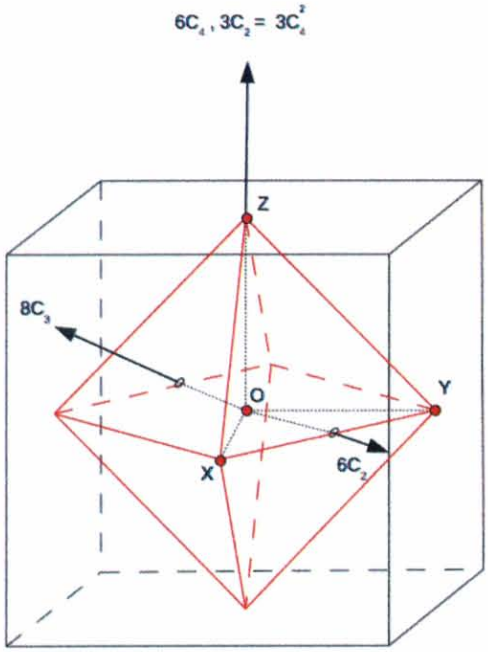


Figure 4.1: Rotational symmetries of a regular octahedron[20].

Fig.(4.1)). It has 24 elements: the identity $E$, three $C_2$ ($180^o$) rotations about the $x$ and $y$ and $z$ axes, eight $C_3$ ($120^o$) about the cubic body diagonals, six $C_4$ ($90^o$) rotations about $x$ and $y$ and $z$ and six $C_2$ rotations through origin parallel to the face diagonals (We use notation as in M. Tinkham [20]). $O_h$ is the full octahedral group with inversion, which is the direct product of inversion $i$ the and octahedral group: $O_h = O \times i$. $O_h$ is the largest point group. It has 48 elements. A *character table* is a table whose rows correspond to irreducible group representations, and columns correspond to classes of group elements. The entries consist of characters, the trace of the matrices representing group elements for each irreducible representation. The character table of $O_h$ is shown in Table (4.1).

| $O_h$ | $E$ | $8C_3$ | $3C_2$ | $6C_2'$ | $6C_4$ | $I$ | $8IC_3$ | $3IC_2$ | $6IC_2'$ | $6IC_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $A_{1g}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $A_{2g}$ | 1 | 1 | -1 | -1 | 1 | 1 | -1 | 1 | 1 | -1 |
| $E_g$ | 2 | -1 | 0 | 0 | 2 | 2 | 0 | -1 | 2 | 0 |
| $T_{1g}$ | 3 | 0 | -1 | 1 | -1 | 3 | 1 | 0 | -1 | -1 |
| $T_{2g}$ | 3 | 0 | 1 | -1 | -1 | 3 | -1 | 0 | -1 | 1 |
| $A_{1u}$ | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 |
| $A_{2u}$ | 1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 |
| $E_u$ | 2 | -1 | 0 | 0 | 2 | -2 | 0 | 1 | -2 | 0 |
| $T_{1u}$ | 3 | 0 | -1 | 1 | -1 | -3 | -1 | 0 | 1 | 1 |
| $T_{2u}$ | 3 | 0 | 1 | -1 | -1 | -3 | 1 | 0 | 1 | -1 |

Table 4.1: The character table of the point group $O_h$.

With four Er ions per unit cell, there is a 16-fold degeneracy of the ground state for each unit cell. The collective angular momentum states can be written as

$$|\pm\pm\pm\pm\rangle \equiv |\pm\rangle_1 \bigotimes |\pm\rangle_2 \bigotimes |\pm\rangle_3 \bigotimes |\pm\rangle_4 \tag{4.30}$$

where subscripts indicate the site number. These states are divided according to representations by which they transform under the operations of octahedral point group $O_h$, which is the point group of the crystal, as $A_{1g} \oplus 3E_g \oplus 2T_{1g} \oplus T_{2g}$ a singlet, 3 doublets and 3 triplets). The states are listed in Table 4.2 [21]. As we always refer to even representation we omit the subscript $g$.

## 4.3 Exchange Hamiltonian with Fd$\bar{3}$m Symmetry

The space group Fd$\bar{3}$m permits a total of four nearest neighbour exchange interactions. There are four distinct exchange terms that are invariant under all the operations of Fd$\bar{3}$m. These terms are listed in Table 4.2, where $X_i$ is the $i$th exchange term for a single tetrahedron. In Table 4.2, $\vec{J}_i$ is the total angular momentum operator for the $i$th Er site in the primitive unit cell. The axes of $\vec{J}$ are chosen such that $J_z$ points in the direction of the $C_3$ site symmetry axis at each site, *i.e.* $J_{1z}$ points in the [111] direction, etc. (see Figure 1.4). The local $x$ and $y$ axes are chosen to obey the right-hand rule. The terms listed in Table 4.2 can be extended to the entire lattice by applying all fcc lattice translations. As discussed in Section 1.4, there are 12 exchange paths in each primitive unit cell. These can be divided into two groups, corresponding to the edges of A tetrahedra and B tetrahedra. These two contributions are the same (have the same coupling constants) when the space group is Fd$\bar{3}$m. So the Hamiltonian can be written as

$$H_{ex} = H_A + H_B \tag{4.31}$$

where $H_A$ is the Hamiltonian of $A$ type tetrahedra. In general, $H_A$ can be written as

$$H_A = \sum_k C_{Ai} X_{ik} \tag{4.32}$$

Where $C_{Ai}$ is the $i$th coupling constant for an A type tetrahedon and $X_{ik}$ $i$th exchange term on the $k$th tetrahedron. $k$ is summed over fcc lattice sites. $\mathrm{H}_B$ is the Hamiltonian of B type tetrahedra. $H_B$ also have the same form of (4.32) with $\mathrm{C}_B$ instead of $\mathrm{C}_A$. The eigenstates of $H_A$ and $H_B$ can be found and are Dirac product of the states of a single tetrahedron, which are given in Table (4.2). However, in general $H_A$ and $H_B$ do not necessarily commute; they may have common eigenfunctions but generally they do not. But the experiments agree with the single tetrahedra picture. Thus the single tetrahedra picture is difficult to justify. A suggestion was made by Ref. [24] that $H_A$ and $H_B$ might have different coupling

constants such that the smaller part (say $H_B$) be treated perturbatively. The difference between the exchange interaction coupling constants implies that there is a structural lattice distortion which makes A tetrahedra smaller and the B tetrahedra larger. It is possible that a very small lattice distortion may produce a noticeable difference in between the coupling constants.

Interactions in Table (4.3) lift the sixteen-fold degeneracy and split the states into a singlet, three doublets and three triplets, which are depicted in Table (4.2). By convention singlets are shown by **A**, doublets by **E**, and triplets by **T**. The correspondence between the states in Table (4.2) and our direct product states are shown in Table (5.1) in following chapter. In following chapter, we use the results we found from group theory together with perturbation theory in order to find the ground states of the system.

| |
|---|
| $\|A_1\rangle = (\|++--\rangle + \|+-+-\rangle + \|+--+\rangle$ |
| $\quad +\|-++-\rangle + \|-+-+\rangle + \|--++\rangle)/\sqrt{6}$ |
| $\|E_+^{(1)}\rangle = \|++++\rangle$ |
| $\|E_-^{(1)}\rangle = \|----\rangle$ |
| $\|E_+^{(2)}\rangle = (\|+---\rangle + \|-+--\rangle + \|--+-\rangle + \|---+\rangle)/2$ |
| $\|E_-^{(2)}\rangle = -(\|+++-\rangle + \|++-+\rangle + \|+-++\rangle + \|-+++\rangle)/2$ |
| $\|E_+^{(3)}\rangle = (\|++--\rangle + \varepsilon\|+-+-\rangle + \varepsilon^2\|+--+\rangle$ |
| $\quad +\|-++-\rangle + \varepsilon\|-+-+\rangle + \varepsilon^2\|--++\rangle)\sqrt{6}$ |
| $\|E_-^{(3)}\rangle = \text{c.c.}$ |
| $\|T_{1x}^{(1)}\rangle = (\varepsilon^2[-\|+++-\rangle + \|++-+\rangle + \|+-++\rangle - \|-+++\rangle]$ |
| $\quad -\varepsilon[\|+---\rangle - \|-+--\rangle - \|--+-\rangle + \|---+\rangle])/2\sqrt{2}$ |
| $\|T_{1y}^{(1)}\rangle = (\varepsilon[\|+++-\rangle - \|++-+\rangle + \|+-++\rangle - \|-+++\rangle]$ |
| $\quad -\varepsilon^2[\|+---\rangle - \|-+--\rangle + \|--+-\rangle - \|---+\rangle])/2\sqrt{2}$ |
| $\|T_{1z}^{(1)}\rangle = (\|+++-\rangle + \|++-+\rangle - \|+-++\rangle - \|-+++\rangle$ |
| $\quad -\|+---\rangle - \|-+--\rangle + \|--+-\rangle + \|---+\rangle)/2\sqrt{2}$ |
| $\|T_{1x}^{(2)}\rangle = (\|+--+\rangle - \|-++-\rangle)/\sqrt{2}$ |
| $\|T_{1y}^{(2)}\rangle = (\|+-+-\rangle - \|-+-+\rangle)/\sqrt{2}$ |
| $\|T_{1z}^{(2)}\rangle = (\|++--\rangle - \|--++\rangle)/\sqrt{2}$ |
| $\|T_{2x}\rangle = (\varepsilon^2[-\|+++-\rangle + \|++-+\rangle + \|+-++\rangle - \|-+++\rangle]$ |
| $\quad +\varepsilon[\|+---\rangle - \|-+--\rangle - \|--+-\rangle + \|---+\rangle])/2\sqrt{2}$ |
| $\|T_{2y}\rangle = (\varepsilon[\|+++-\rangle - \|++-+\rangle + \|+-++\rangle - \|-+++\rangle]$ |
| $\quad +\varepsilon^2[\|+---\rangle - \|-+--\rangle + \|--+-\rangle - \|---+\rangle])/2\sqrt{2}$ |
| $\|T_{2z}\rangle = (\|+++-\rangle + \|++-+\rangle - \|+-++\rangle - \|-+++\rangle$ |
| $\quad +\|+---\rangle + \|-+--\rangle - \|--+-\rangle - \|---+\rangle)/2\sqrt{2}$ |

Table 4.2: Basis functions for the four Er ion sites comprising a single tetrahedron, labelled according to the irreducible representations of $O_h$ by which they transform $\varepsilon = \exp(2\pi i/3)$.

| term | $X_1$ | $X_2$ |
|---|---|---|
| $\vec{J}_1 \cdot \vec{J}_2$ | $-\frac{1}{3}J_{1z}J_{2z}$ | $-\frac{\sqrt{2}}{3}[J_{1z}(J_{2+}+J_{2-})+(J_{1+}+J_{1-})J_{2z}]$ |
| $\vec{J}_3 \cdot \vec{J}_4$ | $-\frac{1}{3}J_{3z}J_{4z}$ | $-\frac{\sqrt{2}}{3}[J_{3z}(J_{4+}+J_{4-})+(J_{3+}+J_{3-})J_{4z}]$ |
| $\vec{J}_1 \cdot \vec{J}_3$ | $-\frac{1}{3}J_{1z}J_{3z}$ | $-\frac{\sqrt{2}}{3}[J_{1z}(\varepsilon J_{3+}+\varepsilon^2 J_{3-})+(\varepsilon J_{1+}+\varepsilon^2 J_{1-})J_{3z}]$ |
| $\vec{J}_2 \cdot \vec{J}_4$ | $-\frac{1}{3}J_{2z}J_{4z}$ | $-\frac{\sqrt{2}}{3}[J_{2z}(\varepsilon J_{4+}+\varepsilon^2 J_{4-})+(\varepsilon J_{2+}+\varepsilon^2 J_{2-})J_{4z}]$ |
| $\vec{J}_1 \cdot \vec{J}_4$ | $-\frac{1}{3}J_{1z}J_{4z}$ | $-\frac{\sqrt{2}}{3}[J_{1z}(\varepsilon^2 J_{4+}+\varepsilon J_{4-})+(\varepsilon^2 J_{1+}+\varepsilon J_{1-})J_{4z}]$ |
| $\vec{J}_2 \cdot \vec{J}_3$ | $-\frac{1}{3}J_{2z}J_{3z}$ | $-\frac{\sqrt{2}}{3}[J_{2z}(\varepsilon^2 J_{3+}+\varepsilon J_{3-})+(\varepsilon^2 J_{2+}+\varepsilon J_{2-})J_{3z}]$ |
| term | $X_3$ | $X_4$ |
| $\vec{J}_1 \cdot \vec{J}_2$ | $\frac{1}{3}(J_{1+}J_{2+}+J_{1-}J_{2-})$ | $-\frac{1}{6}(J_{1+}J_{2-}+J_{1-}J_{2+})$ |
| $\vec{J}_3 \cdot \vec{J}_4$ | $\frac{1}{3}(J_{3+}J_{4+}+J_{3-}J_{4-})$ | $-\frac{1}{6}(J_{3+}J_{4-}+J_{3-}J_{4+})$ |
| $\vec{J}_1 \cdot \vec{J}_3$ | $\frac{1}{3}(\varepsilon^2 J_{1+}J_{3+}+\varepsilon J_{1-}J_{3-})$ | $-\frac{1}{6}(J_{1+}J_{3-}+J_{1-}J_{3+})$ |
| $\vec{J}_2 \cdot \vec{J}_4$ | $\frac{1}{3}(\varepsilon^2 J_{2+}J_{4+}+\varepsilon J_{2-}J_{4-})$ | $-\frac{1}{6}(J_{2+}J_{4-}+J_{2-}J_{4+})$ |
| $\vec{J}_1 \cdot \vec{J}_4$ | $\frac{1}{3}(\varepsilon J_{1+}J_{4+}+\varepsilon^2 J_{1-}J_{4-})$ | $-\frac{1}{6}(J_{1+}J_{4-}+J_{1-}J_{4+})$ |
| $\vec{J}_2 \cdot \vec{J}_3$ | $\frac{1}{3}(\varepsilon J_{2+}J_{3+}+\varepsilon^2 J_{2-}J_{3-})$ | $-\frac{1}{6}(J_{2+}J_{3-}+J_{2-}J_{3+})$ |

Table 4.3: The Heisenberg-Dirac Hamiltonian for a single tetrahedron in terms of local coordinates for each Er ion. The first column lists the terms in H over a single tetrahedron $\varepsilon = \exp\frac{2i\pi}{3}$. The sum of terms in each blocks yields a symmetry allowed term in the exchange interaction, and the sum of all terms is the isotropic exchange interaction $X = \sum_{\langle ij \rangle} \vec{J}_i.\vec{J}_j$

# Chapter 5

# Results and Discussion

**I can live with doubt, and uncertainty, and not knowing. I think it's much more interesting to live not knowing than to have answers which might be wrong. I have approximate answers, and possible beliefs, and different degrees of certainty about different things, but I'm not absolutely sure of anything, and in many things I don't know anything about, such as whether it means anything to ask why we're here, and what the question might mean. I might think about a little, but if I can't figure it out, then I go to something else. But I don't have to know an answer. I don't feel frightened by not knowing things, by being lost in a mysterious universe without having any purpose, which is the way it really is, as far as I can tell, possibly. It doesn't frighten me.** Richard P. Feynman

## 5.1 Single Tetrahedron

In the case of single tetrahedron, we have the four sites depicted in Figure 1.5 the spins can be either up or down. Using (4.31), we can build up 16 possible different states which are shown in the second column of Table 5.1. The first column is the number assigned to these

states according to the following procedure. As we discussed at the beginning of chapter 2, measurement of spin in any direction would result only in up or down state, and nothing in between. In order to do the calculations using a computer we have to build up the states $|\pm\rangle_i$ also their direct product in a way which can be implemented on a computer. Considering $|+\rangle$ as an array (1,0) and $|-\rangle$ as (0,1) enables a 4-site state to be expressed as a $16 \times 1$ array consisting of all zeros save one. For instance, if we want to build up the state $|++-+\rangle$ as an array of numbers we use:

$$|+\rangle \bigotimes |+\rangle \bigotimes |-\rangle \bigotimes |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \bigotimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} \bigotimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} \bigotimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} \tag{5.1}$$

In this case there is a one row number 3 and all the others are zero, so we label this state No. 3. All the other states can be built and labelled in the same manner.

| No. | State | $E_+^{(1)}$ | $E_+^{(2)}$ | $E_+^{(3)}$ | $E_-^{(1)}$ | $E_-^{(2)}$ | $E_-^{(3)}$ | $T_{1z}^{(1)}$ | $T_{2z}$ | $T_{1z}^{(2)}$ | $T_{1x}^{(1)}$ | $T_{2x}$ | $T_{1x}^{(2)}$ | $T_{1y}^{(1)}$ | $T_{2y}$ | $T_{1y}^{(2)}$ | $A$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $\|++++\rangle$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | $\|+++-\rangle$ | 0 | 0 | 0 | 0 | $\frac{-1}{2}$ | 0 | $\frac{1}{\sqrt{8}}$ | $\frac{1}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon}{\sqrt{8}}$ | $\frac{-\varepsilon}{\sqrt{8}}$ | 0 | $\frac{\varepsilon^2}{\sqrt{8}}$ | $\frac{\varepsilon^2}{\sqrt{8}}$ | 0 | 0 |
| 3 | $\|++-+\rangle$ | 0 | 0 | 0 | 0 | $\frac{-1}{2}$ | 0 | $\frac{1}{\sqrt{8}}$ | $\frac{1}{\sqrt{8}}$ | 0 | $\frac{\varepsilon}{\sqrt{8}}$ | $\frac{\varepsilon}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon^2}{\sqrt{8}}$ | $\frac{-\varepsilon^2}{\sqrt{8}}$ | 0 | 0 |
| 4 | $\|++--\rangle$ | 0 | 0 | $\frac{1}{\sqrt{6}}$ | 0 | 0 | $\frac{1}{\sqrt{6}}$ | 0 | 0 | $\frac{1}{\sqrt{2}}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{6}}$ |
| 5 | $\|+-++\rangle$ | 0 | 0 | 0 | 0 | $\frac{-1}{2}$ | 0 | $\frac{-1}{\sqrt{8}}$ | $\frac{-1}{\sqrt{8}}$ | 0 | $\frac{\varepsilon}{\sqrt{8}}$ | $\frac{\varepsilon}{\sqrt{8}}$ | 0 | $\frac{\varepsilon^2}{\sqrt{8}}$ | $\frac{\varepsilon^2}{\sqrt{8}}$ | 0 | 0 |
| 6 | $\|+-+-\rangle$ | 0 | 0 | $\frac{\varepsilon}{\sqrt{6}}$ | 0 | 0 | $\frac{\varepsilon^2}{\sqrt{6}}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{6}}$ |
| 7 | $\|+--+\rangle$ | 0 | 0 | $\frac{\varepsilon^2}{\sqrt{6}}$ | 0 | 0 | $\frac{\varepsilon}{\sqrt{6}}$ | 0 | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{2}}$ | 0 | 0 | 0 | $\frac{1}{\sqrt{6}}$ |
| 8 | $\|+---\rangle$ | 0 | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | $\frac{-1}{\sqrt{8}}$ | $\frac{1}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon^2}{\sqrt{8}}$ | $\frac{\varepsilon^2}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon}{\sqrt{8}}$ | $\frac{\varepsilon}{\sqrt{8}}$ | 0 | 0 |
| 9 | $\|-+++\rangle$ | 0 | 0 | 0 | 0 | $\frac{-1}{2}$ | 0 | $\frac{-1}{\sqrt{8}}$ | $\frac{-1}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon}{\sqrt{8}}$ | $\frac{-\varepsilon}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon^2}{\sqrt{8}}$ | $\frac{-\varepsilon^2}{\sqrt{8}}$ | 0 | 0 |
| 10 | $\|-++-\rangle$ | 0 | 0 | $\frac{\varepsilon^2}{\sqrt{6}}$ | 0 | 0 | $\frac{\varepsilon}{\sqrt{6}}$ | 0 | 0 | 0 | 0 | 0 | $\frac{-1}{\sqrt{2}}$ | 0 | 0 | 0 | $\frac{1}{\sqrt{6}}$ |
| 11 | $\|-+-+\rangle$ | 0 | 0 | $\frac{\varepsilon}{\sqrt{6}}$ | 0 | 0 | $\frac{\varepsilon^2}{\sqrt{6}}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\frac{-1}{\sqrt{2}}$ | $\frac{1}{\sqrt{6}}$ |
| 12 | $\|-+--\rangle$ | 0 | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | $\frac{-1}{\sqrt{8}}$ | $\frac{1}{\sqrt{8}}$ | 0 | $\frac{\varepsilon^2}{\sqrt{8}}$ | $\frac{-\varepsilon^2}{\sqrt{8}}$ | 0 | $\frac{\varepsilon}{\sqrt{8}}$ | $\frac{-\varepsilon}{\sqrt{8}}$ | 0 | 0 |
| 13 | $\|--++\rangle$ | 0 | 0 | $\frac{1}{\sqrt{6}}$ | 0 | 0 | $\frac{1}{\sqrt{6}}$ | 0 | 0 | $\frac{-1}{\sqrt{2}}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{6}}$ |
| 14 | $\|--+-\rangle$ | 0 | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{8}}$ | $\frac{-1}{\sqrt{8}}$ | 0 | $\frac{\varepsilon^2}{\sqrt{8}}$ | $\frac{-\varepsilon^2}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon}{\sqrt{8}}$ | $\frac{\varepsilon}{\sqrt{8}}$ | 0 | 0 |
| 15 | $\|---+\rangle$ | 0 | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{8}}$ | $\frac{-1}{\sqrt{8}}$ | 0 | $\frac{-\varepsilon^2}{\sqrt{8}}$ | $\frac{\varepsilon^2}{\sqrt{8}}$ | 0 | $\frac{\varepsilon}{\sqrt{8}}$ | $\frac{-\varepsilon}{\sqrt{8}}$ | 0 | 0 |
| 16 | $\|----\rangle$ | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table 5.1: The basis states, their label numbers and the overlap they have with singlets, doublets and triplets defined in Table 4.2 . These numbers define the transformation matrix **S**.

We can also build the operators needed in the Hamiltonian by direct products of Pauli matrices and the identity matrix. The following is an example of an operator which acts on site 3 while leaving the others unchanged:

$$J_{3y} = I \bigotimes I \bigotimes \sigma_y \bigotimes I \tag{5.2}$$

which is a $16 \times 16$ matrix:

$$J_{3y} = \begin{pmatrix}
0 & 0 & -i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & 0
\end{pmatrix} \tag{5.3}$$

The following are the identities which are used to do build up the operators in the Hamiltonian given in Table 4.3 [25].

$$J_{\pm} = J_x \pm \imath J_y \tag{5.4}$$

$$\langle \pm | J_z | \pm \rangle = \pm j \tag{5.5}$$

$$\langle \pm | J_{\pm} | \mp \rangle = t \tag{5.6}$$

$j$ and $t$ are numbers that can be calculated using the explicit form of $|\pm\rangle$ given in (1.1). But in the following we leave them as free parameters. Using our transformation matrix $\mathbf{S}$ which is given in the Table 5.1, and our $(16 \times 16)$ Hamiltonian built up as explained, we can find the block diagonal Hamiltonian which is $\mathbf{S}^{-1} H_A \mathbf{S}$ that has 2 identical blocks for doublets, 3 identical Blocks for triplets, and one diagonal element for the single [25]:

$$E = \begin{pmatrix} -2j^2 C_1 & 0 & \sqrt{\frac{2}{3}} t^2 C_3 \\ 0 & -\frac{1}{2} t^2 C_4 & -\frac{4jtC_2}{\sqrt{3}} \\ \sqrt{\frac{2}{3}} t^2 C_3 & -\frac{4jtC_2}{\sqrt{3}} & \frac{1}{3}\left(2j^2 C_1 + t^2 C_4\right) \end{pmatrix} \tag{5.7}$$

$$T = \begin{pmatrix} \frac{1}{6} t^2 \left(4C_3 + C_4\right) & 0 & \frac{4}{3}\sqrt{2} jtC_2 \\ 0 & \frac{1}{6} t^2 \left(-4C_3 + C_4\right) & 0 \\ \frac{4}{3}\sqrt{2} jtC_2 & 0 & \frac{2j^2 C_1}{3} \end{pmatrix} \tag{5.8}$$

$$A = \frac{2}{3}\left(j^2 C_1 - t^2 C_4\right) \tag{5.9}$$

### 5.1.1 Ground State of a Single Tetrahedron

In order to find the ground state, we have to attribute some numbers to the variables in each case. We assume $j = t = 1$, (they get incorporated into the $C_i$'s) and then switch two of the four interactions on at a time in order to find the ground state for the various interaction ratios [25]. These results are shown in Figure 5.1 to 5.6.

The problem simply is finding the eigenvalues and eigenvectors of the matrices introduced,

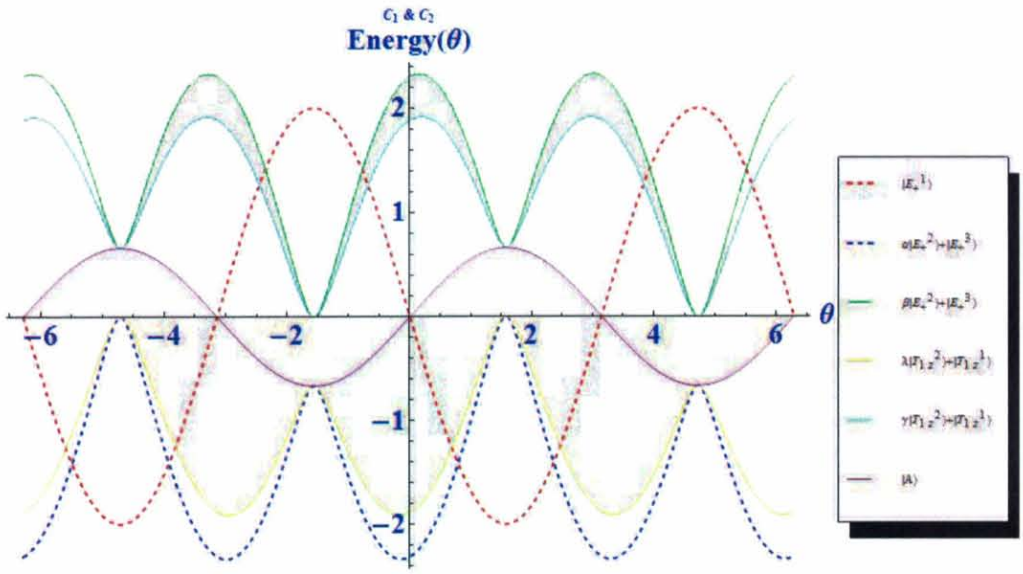


Figure 5.1: Energy as a function of $\theta$ for $C_1 = \sin\theta, C_2 = \cos\theta, C_3 = C_4 = 0$ .

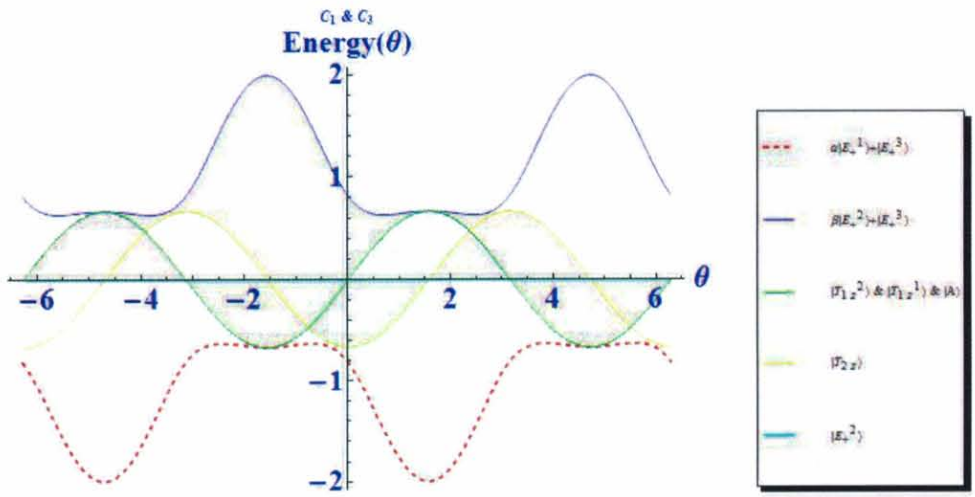


Figure 5.2: Energy as a function of $\theta$ for $C_1 = \sin\theta, C_3 = \cos\theta, C_2 = C_4 = 0$.

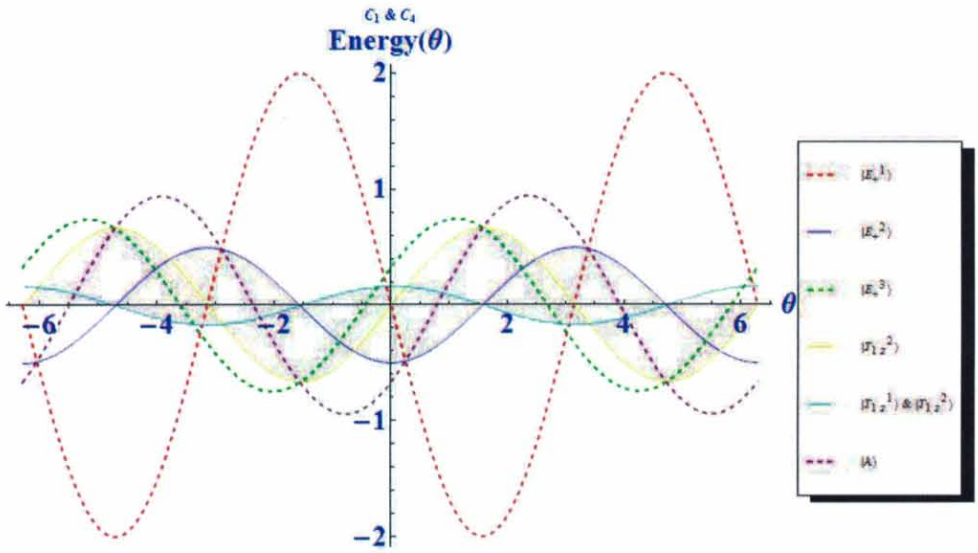


Figure 5.3: Energy as a function of $\theta$ for $C_1 = \sin\theta, C_4 = \cos\theta, C_2 = C_3 = 0$.

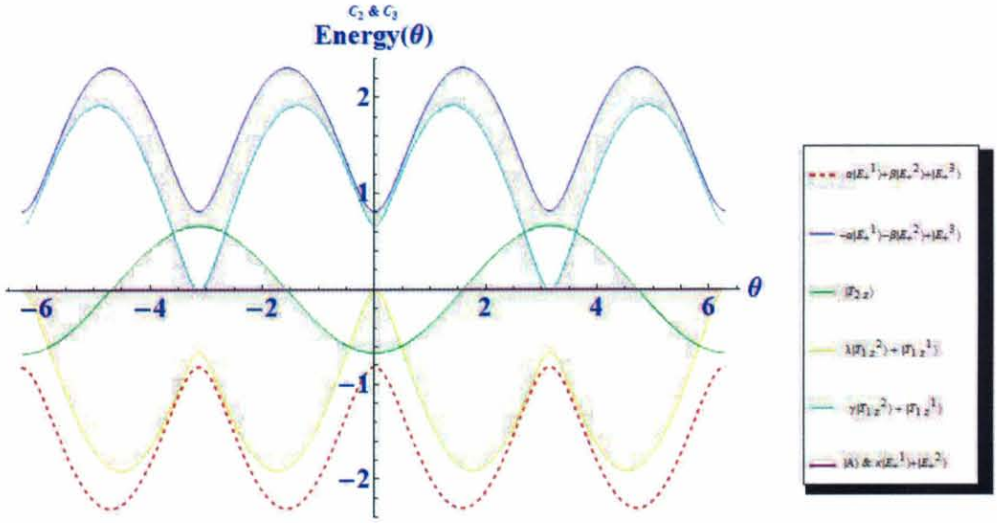


Figure 5.4: Energy as a function of $\theta$ for $C_2 = \sin\theta, C_3 = \cos\theta, C_1 = C_4 = 0$.

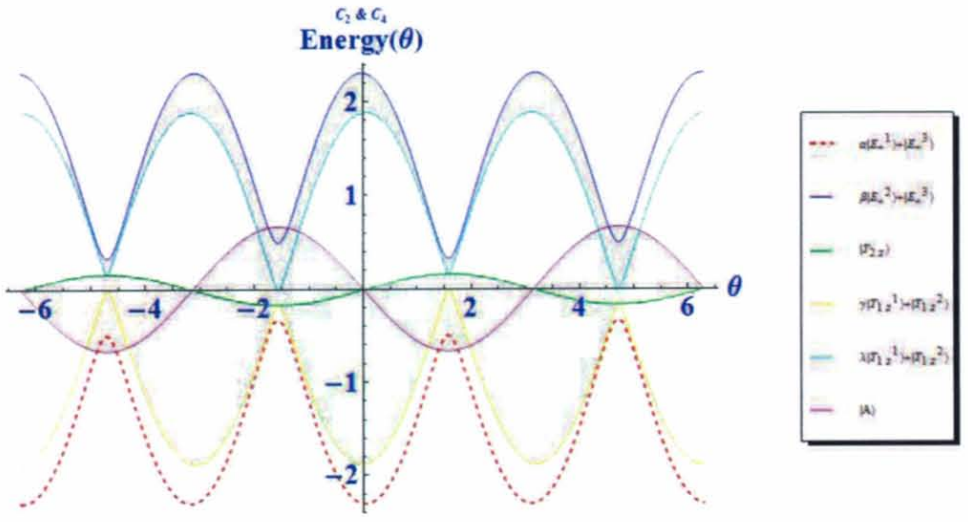


Figure 5.5: Energy as a function of $\theta$ for $C_2 = \sin\theta, C_4 = \cos\theta, C_1 = C_3 = 0$ .

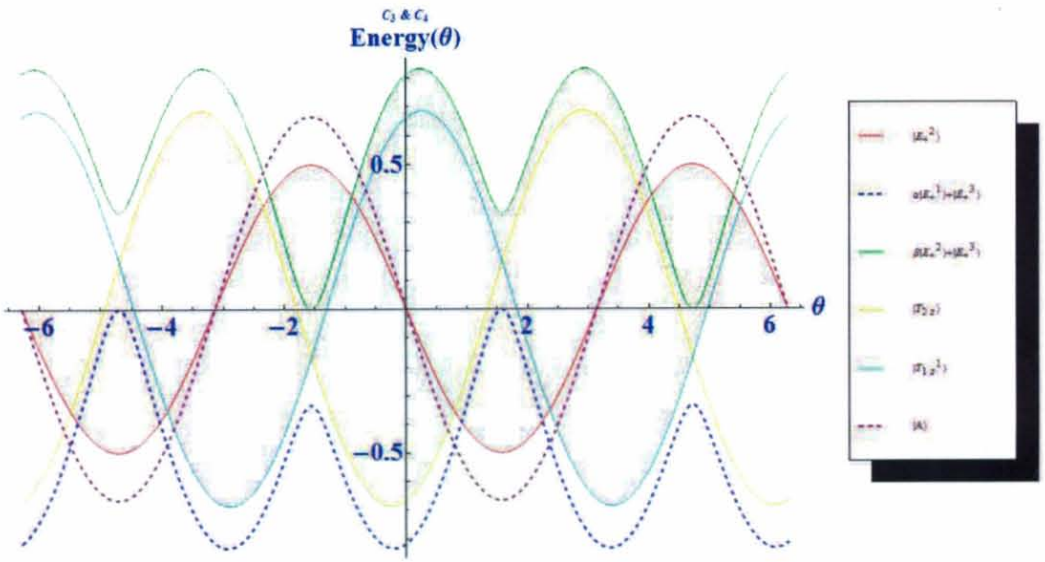


Figure 5.6: Energy as a function of $\theta$ for $C_3 = \sin\theta, C_4 = \cos\theta, C_1 = C_2 = 0$.

however with so many parameters, the general solution is not very enlightening. Instead of the general case, one can consider some interactions in Hamiltonian to be more important or more dominant than the others by switching some interaction on or off. The binary switch will let us do so, and considering all the six possible cases will help us to investigate the problem. We also use the convention of $\frac{\hbar}{2} = 1$ without the loss in generality of the problem. As shown in Figure 5.1 [25], if we set $C_3$=$C_4$=0 and let the $C_1$ vary as a function sine and $C_2$ as a cosine function, the ground state is doubly degenerate $(\alpha|E_{\pm}^{(2)}\rangle + |E_{\pm}^{(3)}\rangle)$ where $\alpha = \frac{C_1+\sqrt{C_1^2+48C_2^2}}{4\sqrt{3}C_2}$. As the $C_1$ and $C_2$ vary like sine and cosine respectively, the ground state energy will mainly follow the blue dashed line. For some specific values of the sine and cosine argument $(\theta)$, the ground state will become degenerate with the singlet or the triplet. In Figure 5.2, which has $C_2 = C_4$ =0, the ground state is again a linear combination of doublets, but a different one with different coefficients which follows the red dashed line. The green line representing three different states with the same energy that becomes degenerate with ground states for specific values of periodic functions.

With $C_2 = C_3 = 0$ shown in Figure 5.3, interestingly there are three different candidates for the ground states for different values of $\theta$.The singlet or the doublets are three different candidates for ground state in this cases.

As for the case $C_1 = C_4 = 0$ shown in Figure 5.4, the ground state is mainly a linear combination of doublet states that are degenerate with triplets in some values of the $\theta$ ($C_2$ = 0 and $C_3$ = -1) . If we want to be more specific on this case, only to see how the states would look like exactly, the ground state is [25]:

$$\alpha|E_{+}^{(1)}\rangle + \beta|E_{+}^{(2)}\rangle + |E_{+}^{(3)}\rangle \tag{5.10}$$

where

$$\alpha = -\frac{C_3}{\sqrt{8C_2^2 + C_3^2}} \qquad \beta = \frac{2\sqrt{2}C_2}{\sqrt{8C_2^2 + C_3^2}} \tag{5.11}$$

The linear combination of triplet states which sometimes is degenerate with the ground state in this case is of the form:

$$\lambda|T_{1z}^{(2)}\rangle + |T_{1z}^{(1)}\rangle \tag{5.12}$$

where:

$$\lambda = -\frac{-C_3 + \sqrt{32C_2^2 + C_3^2}}{4\sqrt{2}C_2} \tag{5.13}$$

Figure 5.5 and Figure 5.6 show the other two possible cases in this binary investigation of the ground states with respect to the coupling constants. Table 5.2 lists the ground states (doublets) for all cases.

| Nonzero C's | Ground States | $\alpha$ | $\beta$ | Figure |
|---|---|---|---|---|
| $C_1$ & $C_2$ | $(\alpha\|E_+^{(2)}\rangle + \|E_+^{(3)}\rangle)$ | $\frac{C_1+\sqrt{C_1^2+48C_2^2}}{4\sqrt{3}C_2}$ | - | (5.1) |
| $C_1$ & $C_3$ | $(\alpha\|E_+^{(1)}\rangle + \|E_+^{(3)}\rangle)$ | $-\frac{4C_1+\sqrt{2}\sqrt{8C_1^2+3C_3^2}}{\sqrt{6}C_3}$ | - | (5.2) |
| $C_1$ & $C_4$ | $(\|E_+^{(1)}\rangle)$ or $(\|E_+^{(3)}\rangle)$ or $(\|A\rangle)$ | - | - | (5.3) |
| $C_2$ & $C_3$ | $(\alpha\|E_+^{(1)}\rangle + \beta\|E_+^{(2)}\rangle + \|E_+^{(3)}\rangle)$ | $-\frac{C_3}{\sqrt{8C_2^2+C_3^2}}$ | $\frac{2\sqrt{2}C_2}{\sqrt{8C_2^2+C_3^2}}$ | (5.4) |
| $C_2$ & $C_4$ | $(\alpha\|E_+^{(1)}\rangle + \|E_+^{(3)}\rangle)$ | $\frac{5C_4-\sqrt{768C_2^2+25C_4^2}}{16\sqrt{3}C_2}$ | - | (5.5) |
| $C_3$ & $C_4$ | $(\alpha\|E_+^{(1)}\rangle + \|E_+^{(3)}\rangle)$ or $(\|A\rangle)$ | $\frac{1}{6}\left(C_4 - \sqrt{24C_3^2 + C_4^2}\right)$ | - | (5.6) |

Table 5.2: The possible ground states when only two of four coupling constants are zero. The ground states are mainly doublets [25].

## 5.2 Two Tetrahedra

If we consider two tetrahedra, the state that describe the system should carry the information needed to specify the spin configuration on 8 sites. According to what we did previously, we

can build up the states as follows:

$$|\pm\pm\pm\pm\pm\pm\pm\pm\rangle \equiv |\pm\rangle_1 \bigotimes |\pm\rangle_2 \bigotimes |\pm\rangle_3 \bigotimes |\pm\rangle_4 \bigotimes |\pm\rangle_5 \bigotimes |\pm\rangle_6 \bigotimes |\pm\rangle_7 \bigotimes |\pm\rangle_8 \quad (5.14)$$

Again by considering the $|+\rangle$ being (1,0) and $|-\rangle$ being (0,1), one can build up 256 distinct states which are of the form $256 \times 1$ array in which all elements are zero save one. The Hamiltonian $H_A$ can also be built up by the direct product of the Pauli spin matrices and identity matrix on each site. Suppose we need to measure the **Y** direction of spin on the site labelled as 7 (See Figure 5.7. The operator for this case is $J_{7y}$ which is a $256 \times 256$ matrix that is built as follows:

$$J_{7y} = I \bigotimes I \bigotimes I \bigotimes I \bigotimes I \bigotimes I \bigotimes \sigma_y \bigotimes I \quad (5.15)$$

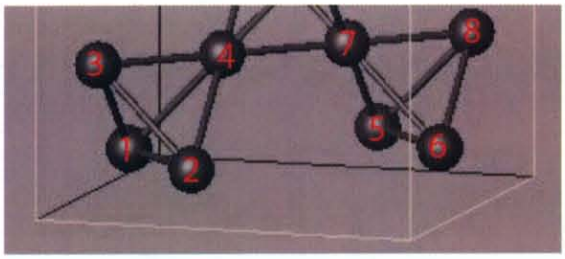


Figure 5.7: Two tetrahedra with sites labelled by the convention used throughout this chapter.

If we define the Hamiltonian on first tetrahedron $H_A = C_1X_1 + C_2X_2 + C_3X_3 + C_4X_4$ and on second one $H_{A'} = C_1Y_1 + C_2Y_2 + C_3Y_3 + C_4Y_4$, where the terms in Hamiltonian are given by:

$$X_1 = -\tfrac{1}{3}\left(J_{1z}.J_{2z} + J_{3z}.J_{4z} + J_{1z}.J_{3z} + J_{2z}.J_{4z} + J_{1z}.J_{4z} + J_{2z}.J_{3z}\right)$$

$$Y_1 = -\tfrac{1}{3}\left(J_{5z}.J_{6z} + J_{7z}.J_{8z} + J_{5z}.J_{7z} + J_{6z}.J_{8z} + J_{5z}.J_{8z} + J_{6z}.J_{7z}\right)$$

$$X_2 = -\tfrac{\sqrt{2}}{3}\left(J_{1z}.\left(J_{2P} + J_{2M}\right) + \left(J_{1P} + J_{1M}\right).J_{2z} + J_{3z}.\left(J_{4P} + J_{4M}\right)\right.$$
$$+\left(J_{3P} + J_{3M}\right).J_{4z} + J_{1z}.\left(\epsilon J_{3P} + \epsilon^2 J_{3M}\right) + \left(\epsilon J_{1P} + \epsilon^2 J_{1M}\right).J_{3z} + J_{2z}.\left(\epsilon J_{4P} + \epsilon^2 J_{4M}\right)$$
$$+\left(\epsilon J_{2P} + \epsilon^2 J_{2M}\right).J_{4z} + J_{1z}.\left(\epsilon^2 J_{4P} + \epsilon J_{4M}\right) + \left(\epsilon^2 J_{1P} + \epsilon J_{1M}\right).J_{4z} + J_{2z}.\left(\epsilon^2 J_{3P} + \epsilon J_{3M}\right) +$$
$$\left.\left(\epsilon^2 J_{2P} + \epsilon J_{2M}\right).J_{3z}\right)$$

$$Y_2 = -\tfrac{\sqrt{2}}{3}\left(J_{5z}.\left(J_{6P} + J_{6M}\right) + \left(J_{5P} + J_{5M}\right).J_{6z} + J_{7z}.\left(J_{8P} + J_{8M}\right)\right.$$
$$+\left(J_{7P} + J_{7M}\right).J_{8z} + J_{5z}.\left(\epsilon J_{7P} + \epsilon^2 J_{7M}\right) + \left(\epsilon J_{5P} + \epsilon^2 J_{5M}\right).J_{7z} + J_{6z}.\left(\epsilon J_{8P} + \epsilon^2 J_{8M}\right)$$
$$+\left(\epsilon J_{6P} + \epsilon^2 J_{6M}\right).J_{8z} + J_{5z}.\left(\epsilon^2 J_{8P} + \epsilon J_{8M}\right) + \left(\epsilon^2 J_{5P} + \epsilon J_{5M}\right).J_{8z}$$
$$\left.+\mathrm{J}_{6z}.\left(\epsilon^2 J_{7P} + \epsilon J_{7M}\right) + \left(\epsilon^2 J_{6P} + \epsilon J_{6M}\right).J_{7z}\right)$$

$$X_3 = \tfrac{1}{3}\left(J_{1P}.J_{2P} + J_{1M}.J_{2M} + J_{3P}.J_{4P} + J_{3M}.J_{4M} + \epsilon^2 J_{1P}.J_{3P}\right.$$
$$+\epsilon J_{1M}.J_{3M} + \epsilon^2 J_{2P}.J_{4P} + \epsilon J_{2M}.J_{4M} + \epsilon J_{1P}.J_{4P}$$
$$\left.+\epsilon^2 J_{1M}.J_{4M} + \epsilon J_{2P}.J_{3P} + \epsilon^2 J_{2M}.J_{3M}\right)$$

$$Y_3 = \tfrac{1}{3}\left(J_{5P}.J_{6P} + J_{5M}.J_{6M} + J_{7P}.J_{8P} + J_{7M}.J_{8M} + \epsilon^2 J_{5P}.J_{7P}\right.$$
$$+\epsilon J_{5M}.J_{7M} + \epsilon^2 J_{6P}.J_{8P} + \epsilon J_{6M}.J_{8M} + \epsilon J_{5P}.J_{8P}$$
$$\left.+\epsilon^2 J_{5M}.J_{8M} + \epsilon J_{6P}.J_{7P} + \epsilon^2 J_{6M}.J_{7M}\right)$$

$$X_4 = -\tfrac{1}{6}\left(J_{1P}.J_{2M} + J_{1M}.J_{2P} + J_{3P}.J_{4M} + J_{3M}.J_{4P} + J_{1P}.J_{3M} + J_{1M}.J_{3P}\right.$$
$$\left.+\mathrm{J}_{2P}.J_{4M} + J_{2M}.J_{4P} + J_{1P}.J_{4M} + J_{1M}.J_{4P} + J_{2P}.J_{3M} + J_{2M}.J_{3P}\right)$$

$$Y_4 = -\tfrac{1}{6}\left(J_{5P}.J_{6M} + J_{5M}.J_{6P} + J_{7P}.J_{8M} + J_{7M}.J_{8P} + J_{5P}.J_{7M} + J_{5M}.J_{7P}\right.$$
$$\left.+\mathrm{J}_{6P}.J_{8M} + J_{6M}.J_{8P} + J_{5P}.J_{8M} + J_{5M}.J_{8P} + J_{6P}.J_{7M} + J_{6M}.J_{7P}\right)$$

where P and M subscripts stands for + and − respectively. Each operator is now a 256 × 256 array. We can find the block diagonalized matrix for the case of 8 sites of the form $\mathbf{S}^{-1}(H_A + H_{A'})\mathbf{S}$. For the case of a single tetrahedron, $\mathbf{S}$ which was a 16 × 16 array, which now is replaced by $\mathbf{S} \otimes \mathbf{S}$ which is a 256 × 256 array. However for simplicity we will still keep call it $\mathbf{S}$, keeping in mind that the transformation matrix for states, has larger dimension for larger Hilbert space. The result of $\mathbf{S}^{-1}(H_A + H_{A'})\mathbf{S}$ is a 256 × 256 array which is the sum of the block diagonal matrices $H_A \otimes I + I \otimes H_{A'}$ and some of its matrix elements are shown in Table 5.3. We can diagonalize this Hamiltonian if we pick suitable values for $j$ and $t$ and also two of the coupling constants as before and find the eigenvalues and eigenvectors. The ground states for two tetrahedra is simply the direct product of possible ground states for one tetrahedron. As the ground state is degenerate in the case of one tetrahedra, the order of degeneracy increases when we are dealing with direct product states.

| States | $\|E_+^{(1)}\rangle\|E_+^{(1')}\rangle$ | $\|E_+^{(1)}\rangle\|E_+^{(2')}\rangle$ | $\cdots$ | $\|E_+^{(1)}\rangle\|A'\rangle$ | $\|E_+^{(2)}\rangle\|E_+^{(1')}\rangle$ | $\cdots$ | $\|A\rangle\|A'\rangle$ |
|---|---|---|---|---|---|---|---|
| $\langle E_+^{(1')}\|\langle E_+^{(1)}\|$ | -4 j$^2C_1$ | 0 | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\langle E_+^{(2')}\|\langle E_+^{(1)}\|$ | 0 | -2 j$^2C_1 - \frac{t^2C_4}{2}$ | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\langle E_+^{(3')}\|\langle E_+^{(1)}\|$ | $\sqrt{\frac{2}{3}}t^2C_3$ | $-\frac{4jtC_2}{\sqrt{3}}$ | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\langle E_-^{(1')}\|\langle E_+^{(1)}\|$ | 0 | 0 | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\langle E_-^{(2')}\|\langle E_+^{(1)}\|$ | 0 | 0 | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\vdots$ | $\vdots$ | $\vdots$ | $\cdots$ | $\vdots$ | $\vdots$ | $\cdots$ | $\vdots$ |
| $\langle A'\|\langle E_+^{(1)}\|$ | 0 | 0 | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\langle E_+^{(1')}\|\langle E_+^{(2)}\|$ | 0 | 0 | $\cdots$ | 0 | 0 | $\cdots$ | 0 |
| $\vdots$ | $\vdots$ | $\vdots$ | $\cdots$ | $\vdots$ | $\vdots$ | $\cdots$ | $\vdots$ |
| $\langle A'\|\langle A\|$ | 0 | 0 | $\cdots$ | 0 | 0 | $\cdots$ | $\vdots$ |

Table 5.3: Some matrix elements for the exchange interaction Hamiltonian for 2 tetrahedra [25]. (Full matrix is available by contacting the author)

## 5.3 Two Tetrahedra Perturbed by $H_B$

We have found the exact solution for a system of two isolated tetrahedra. Now we include the exchange interaction for B type tetrahedra in our finite system with periodic boundary conditions perturbatively. We use periodic boundary conditions, so there are two A type tetrahedra and two B type tetrahedra. The atomic position of all eight Er atoms are given in Table (5.4). The A tetrahedra are the sets of atoms A=$\{\mathbf{1},\mathbf{2},\mathbf{3},\mathbf{4}\}$ and A$'$ = $\{\mathbf{5},\mathbf{6},\mathbf{7},\mathbf{8}\}$. We consider two A type tetrahedra and two B type with periodic boundary condition.

It can be verified that the B-type tetrahedra are on sites $\{\mathbf{1},\mathbf{2},\mathbf{4},\mathbf{7}\}$ and $\{\mathbf{3},\mathbf{5},\mathbf{6},\mathbf{8}\}$. The Hamiltonian for B type tetrahdra is of the form H$_B$=$C_5\,(Z_1 + V_1) + C_6\,(Z_2 + V_2) +$

| Tetrahedron # | Atom # | Position |
|---|---|---|
| A | 1 | $(5/8, 1/8, 1/8)$ |
| $+(0,0,0)$ | 2 | $(7/8, 3/8, 1/8)$ |
| | 3 | $(7/8, 1/8, 3/8)$ |
| | 4 | $(5/8, 3/8, 3/8)$ |
| A′ | 5 | $(1/8, 5/8, 1/8)$ |
| $+(-1/2, 1/2, 0)$ | 6 | $(3/8, 7/8, 1/8)$ |
| | 7 | $(3/8, 5/8, 3/8)$ |
| | 8 | $(1/8, 7/8, 3/8)$ |

Table 5.4: Atom positions of eight Er atoms in two tetrahedra

$C_7 (Z_3 + V_3) + C_8 (Z_4 + V_4)$, where

$$\mathrm{Z}_1 = -\tfrac{1}{3} \left( J_{1z}.J_{2z} + J_{7z}.J_{4z} + J_{1z}.J_{7z} + J_{2z}.J_{4z} + J_{1z}.J_{4z} + J_{2z}.J_{7z} \right)$$
$$\mathrm{V}_1 = -\tfrac{1}{3} \left( J_{5z}.J_{6z} + J_{3z}.J_{8z} + J_{5z}.J_{3z} + J_{6z}.J_{8z} + J_{5z}.J_{8z} + J_{6z}.J_{3z} \right)$$

$$\mathrm{Z}_2 = -\tfrac{\sqrt{2}}{3} \left( J_{1z}.\left(J_{2P} + J_{2M}\right) + \left(J_{1P} + J_{1M}\right).J_{2z} + J_{7z}.\left(J_{4P} + J_{4M}\right) \right.$$
$$+\left(J_{7P} + J_{7M}\right).J_{4z} + J_{1z}.\left(\epsilon J_{7P} + \epsilon^2 J_{7M}\right) + \left(\epsilon J_{1P} + \epsilon^2 J_{1M}\right).J_{7z} + J_{2z}.\left(\epsilon J_{4P} + \epsilon^2 J_{4M}\right)$$
$$+\left(\epsilon J_{2P} + \epsilon^2 J_{2M}\right).J_{4z} + J_{1z}.\left(\epsilon^2 J_{4P} + \epsilon J_{4M}\right) + \left(\epsilon^2 J_{1P} + \epsilon J_{1M}\right).J_{4z} + J_{2z}.\left(\epsilon^2 J_{7P} + \epsilon J_{7M}\right) +$$
$$\left. \left(\epsilon^2 J_{2P} + \epsilon J_{2M}\right).J_{7z} \right)$$
$$\mathrm{V}_2 = -\tfrac{\sqrt{2}}{3} \left( J_{5z}.\left(J_{6P} + J_{6M}\right) + \left(J_{5P} + J_{5M}\right).J_{6z} + J_{3z}.\left(J_{8P} + J_{8M}\right) \right.$$
$$+\left(J_{3P} + J_{3M}\right).J_{8z} + J_{5z}.\left(\epsilon J_{3P} + \epsilon^2 J_{3M}\right) + \left(\epsilon J_{5P} + \epsilon^2 J_{5M}\right).J_{3z} + J_{6z}.\left(\epsilon J_{8P} + \epsilon^2 J_{8M}\right)$$
$$+\left(\epsilon J_{6P} + \epsilon^2 J_{6M}\right).J_{8z} + J_{5z}.\left(\epsilon^2 J_{8P} + \epsilon J_{8M}\right) + \left(\epsilon^2 J_{5P} + \epsilon J_{5M}\right).J_{8z} + J_{6z}.\left(\epsilon^2 J_{3P} + \epsilon J_{3M}\right) +$$
$$\left. \left(\epsilon^2 J_{6P} + \epsilon J_{6M}\right).J_{3z} \right)$$

$$Z_3 = \tfrac{1}{3}\,(J_{1P}.J_{2P} + J_{1M}.J_{2M} + J_{7P}.J_{4P} + J_{7M}.J_{4M} + \epsilon^2 J_{1P}.J_{7P}$$
$$+\epsilon J_{1M}.J_{7M} + \epsilon^2 J_{2P}.J_{4P} + \epsilon J_{2M}.J_{4M} + \epsilon J_{1P}.J_{4P} + \epsilon^2 J_{1M}.J_{4M} + \epsilon J_{2P}.J_{7P} + \epsilon^2 J_{2M}.J_{7M})$$
$$V_3 = \tfrac{1}{3}\,(J_{5P}.J_{6P} + J_{5M}.J_{6M} + J_{3P}.J_{8P} + J_{3M}.J_{8M} + \epsilon^2 J_{5P}.J_{3P}$$
$$+\epsilon J_{5M}.J_{3M} + \epsilon^2 J_{6P}.J_{8P} + \epsilon J_{6M}.J_{8M} + \epsilon J_{5P}.J_{8P} + \epsilon^2 J_{5M}.J_{8M} + \epsilon J_{6P}.J_{3P} + \epsilon^2 J_{6M}.J_{3M})$$

$$Z_4 = -\tfrac{1}{6}\,(J_{1P}.J_{2M} + J_{1M}.J_{2P} + J_{7P}.J_{4M} + J_{7M}.J_{4P} + J_{1P}.J_{7M} + J_{1M}.J_{7P}$$
$$+J_{2P}.J_{4M} + J_{2M}.J_{4P} + J_{1P}.J_{4M} + J_{1M}.J_{4P} + J_{2P}.J_{7M} + J_{2M}.J_{7P})$$
$$V_4 = -\tfrac{1}{6}\,(J_{5P}.J_{6M} + J_{5M}.J_{6P} + J_{3P}.J_{8M} + J_{3M}.J_{8P} + J_{5P}.J_{3M} + J_{5M}.J_{3P}$$
$$+J_{6P}.J_{8M} + J_{6M}.J_{8P} + J_{5P}.J_{8M} + J_{5M}.J_{8P} + J_{6P}.J_{3M} + J_{6M}.J_{3P})$$

where P and M subscripts stands for + and − respectively. As mentioned before, the B type tetrahedra appear as a result of different coupling constants between atom sites. So in general C's in B type are different than those in A type tetrahedra. Now we have the total Hamiltonian $H_T$ defined as follows which is the complete Hamiltonian for two tetrahedra with considering the effect of the B type tetrahedra.

$$H_T = H_A + H_{A'} + H_B \tag{5.16}$$

With the addition of $H_B$, diagonalizing the $256 \times 256$ matrix $H_T$ with so many off-diagonal elements would be a difficult task. In order to solve this problem, one approach is to treat the $H_B$ part perturbatively to find the ground state when the B type tetrahedra is present. Generally, the perturbation will mix in the other states with the ground state of system of two tetrahedra.

We use the perturbative method described in Chapter one. As we are dealing mainly with degenerate ground states, we use degenerate perturbation theory (DPT) following the

8 steps introduced in Section (2.4.2). The rest of this Chapter is devoted to the result of perturbative treatment of the B type tetrahedra for a specific value of coupling constants.

### 5.3.1 Degenerate Perturbation Theory for $C_1 = C_4 = \frac{1}{\sqrt{2}}$, $C_2 = C_3 = 0$

As it can be seen from Figure (5.3) at $\theta = \frac{\pi}{4}$, the ground state is mainly $|E_+^{(1)}\rangle$. So the ground state for our unperturbed two tetrahedra system has these four degenerate ground states:

$$|E_+^{(1)}\rangle|E_+^{(1')}\rangle \quad , \quad |E_-^{(1)}\rangle|E_-^{(1')}\rangle \quad , \quad |E_+^{(1)}\rangle|E_-^{(1')}\rangle \quad , \quad |E_-^{(1)}\rangle|E_+^{(1')}\rangle \tag{5.17}$$

The perturbation will lift the degeneracy so that the states split into two slightly different levels.

In doing the perturbation, since we have $C_2 = C_3 = 0$, we also chose the corresponding coupling constants in $H_B$ which are $C_6$ and$C_7$ to be zero, and set the two others to be $\frac{1}{10}$ of the value of $C_1$ and $C_4$ so we that can treat it as a perturbation (the value $\frac{1}{10}$ was chosen for the purpose of doing numerical calculations and can be changed without the loss of generality of the problem). So we have $C_5 = \frac{1}{10}\, C_1$ and $C_8 = \frac{1}{10}\, C_1$. Even by considering this perturbation, states which are related by time reversal symmetry still stay degenerate.

$$(4.21): \begin{cases} |E_+^{(1)}\rangle|E_-^{(1')}\rangle \quad |E_-^{(1)}\rangle|E_+^{(1')}\rangle \quad \rightarrow \quad E = -2.82876 \\ |E_+^{(1)}\rangle|E_+^{(1')}\rangle \quad |E_-^{(1)}\rangle|E_-^{(1')}\rangle \quad \rightarrow \quad E = -3.11127 \end{cases} \tag{5.18}$$

It is interesting to see how higher order in perturbation theory mixes the states. First of all each set of degenerate states related by time reversal symmetry mix the same by the effect of B type tetrahedra as we expected. Furthermore the state $|E_+^{(1)}\rangle|E_+^{(1')}\rangle$ does not mix to the first order in perturbed wave function. However $|E_+^{(1)}\rangle|E_-^{(1')}\rangle$ and its time reversal will mix with the following states [25]:

$$
|E_+^{(1)}\rangle|E_-^{(1')}\rangle \to: \left\{ \begin{array}{l}
|E_+^{(1)}\rangle|E_-^{(1')}\rangle \\
(-0.00833333)|E_-^{(3)}\rangle|E_+^{(3')}\rangle \\
(0.00160706)|E_-^{(3)}\rangle|T'_{2z}\rangle \\
(-0.00160706)|E_-^{(3)}\rangle|T_{1z}^{(2')}\rangle \\
(-0.00080353 - 0.00139176i)|E_-^{(3)}\rangle|T'_{2x}\rangle \\
(0.00080353 + 0.00139176i)|E_-^{(3)}\rangle|T_{1x}^{(2')}\rangle \\
(0.00080353 - 0.00139176i)|E_-^{(3)}\rangle|T'_{2y}\rangle \\
(-0.00080353 + 0.00139176i)|E_-^{(3)}\rangle|T_{1y}^{(2')}\rangle \\
(0.00160706)|T_{1z}^{(1)}\rangle|E_+^{(3)}\rangle \\
(0.000961538)|T_{1z}^{(1)}\rangle|T'_{2z}\rangle \\
(-0.000961538)|T_{1z}^{(1)}\rangle|T_{1z}^{(2')}\rangle \\
(-0.000480769 - 0.000832717i)|T_{1z}^{(1)}\rangle|T'_{2x}\rangle \\
(0.000480769 + 0.000832717i)|T_{1z}^{(1)}\rangle|T_{1x}^{(2')}\rangle \\
(0.000480769 - 0.000832717i)|T_{1z}^{(1)}\rangle|T'_{2y}\rangle \\
(-0.000480769 + 0.000832717i)|T_{1z}^{(1)}\rangle|T_{1y}^{(2')}\rangle \\
(0.00160706)|T_{2z}\rangle|E_+^{(3)}\rangle \\
(0.000961538)|T_{2z}\rangle|T'_{2z}\rangle \\
(-0.000961538)|T_{2z}\rangle|T_{1z}^{(2')}\rangle \\
(-0.000480769 - 0.000832717i)|T_{2z}\rangle|T'_{2x}\rangle \\
(0.000480769 + 0.000832717i)|T_{2z}\rangle|T_{1x}^{(2')}\rangle \\
(0.000480769 - 0.000832717i)|T_{2z}\rangle|T'_{2y}\rangle \\
(-0.000480769 + 0.000832717i)|T_{2z}\rangle|T_{1y}^{(2')}\rangle \\
\vdots
\end{array} \right.
$$

$$
|E_+^{(1)}\rangle|E_-^{(1')}\rangle \rightarrow: \left\{ \begin{array}{l}
\vdots \\
(-0.00080353 + 0.00139176i)|T_{2x}\rangle|E_+^{(3)}\rangle \\
(-0.000480769 + 0.000832717i)|T_{2x}\rangle|T'_{2z}\rangle \\
(0.000480769 - 0.000832717i)|T_{2x}\rangle|T_{1z}^{(2')}\rangle \\
(0.000961538)|T_{2x}\rangle|T'_{2x}\rangle \\
(-0.000961538)|T_{2x}\rangle|T_{1x}^{(2')}\rangle \\
(0.000480769 + 0.000832717i)|T_{2x}\rangle|T'_{2y}\rangle \\
(-0.000480769 - 0.000832717i)|T_{2x}\rangle|T_{1y}^{(2')}\rangle \\
(-0.00080353 + 0.00139176i)|T_{1x}^{(2)}\rangle|E_+^{(3)}\rangle \\
(-0.000480769 + 0.000832717i)|T_{1x}^{(2)}\rangle|T'_{2z}\rangle \\
(0.000480769 - 0.000832717i)|T_{1x}^{(2)}\rangle|T_{1z}^{(2')}\rangle \\
(0.000961538)|T_{1x}^{(2)}\rangle|T'_{2x}\rangle \\
(-0.000961538)|T_{1x}^{(2)}\rangle|T_{1x}^{(2')}\rangle \\
(0.000480769 + 0.000832717i)|T_{1x}^{(2)}\rangle|T'_{2y}\rangle \\
(-0.000480769 - 0.000832717i)|T_{1x}^{(2)}\rangle|T_{1y}^{(2')}\rangle \\
(0.00080353 + 0.00139176i)|T_{2y}\rangle|E_+^{(3)}\rangle \\
(0.000480769 + 0.000832717i)|T_{2y}\rangle|T'_{2z}\rangle \\
(-0.000480769 - 0.000832717i)|T_{2y}\rangle|T_{1z}^{(2')}\rangle \\
(0.000480769 + 0.000832717i)|T_{2y}\rangle|T'_{2x}\rangle \\
(-0.000480769 - 0.000832717i)|T_{2y}\rangle|T_{1x}^{(2')}\rangle \\
(0.000961538)|T_{2y}\rangle|T'_{2y}\rangle \\
(-0.000961538)|T_{2y}\rangle|T_{1y}^{(2')}\rangle \\
\vdots
\end{array} \right.
$$

$$|E_+^{(1)}\rangle|E_-^{(1')}\rangle \rightarrow: \begin{cases} \vdots \\ (0.00080353 + 0.00139176i)|T_{1y}^{(2)}\rangle|E_+^{(3)}\rangle \\ (0.000480769 + 0.000832717i)|T_{1y}^{(2)}\rangle|T'_{2z}\rangle \\ (-0.000480769 - 0.000832717i)|T_{1y}^{(2)}\rangle|T_{1z}^{(2')}\rangle \\ (0.000480769 + 0.000832717i)|T_{1y}^{(2)}\rangle|T'_{2x}\rangle \\ (-0.000480769 - 0.000832717i)|T_{1y}^{(2)}\rangle|T_{1x}^{(2')}\rangle \\ (0.000961538)|T_{1y}^{(2)}\rangle|T'_{2y}\rangle \\ (-0.000961538)|T_{1y}^{(2)}\rangle|T_{1y}^{(2')}\rangle \end{cases}$$

## 5.4 Interpretation of the Results

For any other values of $\theta$, we can pick any two $C$'s and do (DPT) on the corresponding ground states, following the steps described in (2.4.2) to get the split in states and also mixes from the other states. In the most of the cases investigated by the author, the degeneracy of the states which are related to each other with time reversal symmetry were not lifted. However, we did the perturbation theory up to first order correction in the wave-function. Furthermore for different $C$'s, the states that mixes in with the ground state follow a rhythmical pattern apart from the weight of that mixture. This rhythm can also be observed in the case of $C_1$ and $C_4$ at $\theta = \frac{\pi}{4}$. The states and the energies are calculated for 5 different cases and possible to be further developed for any other value of the exchange interaction of interest. From the wave-functions found by perturbation, further information can be extracted. The magnetic transition that $Er_2Ti_2O_7$ shows at 1.2 K is not easy to explain via the unperturbed ground state. The magnetically ordered state has a non-zero expectation value of the operator $M =$ $S_{1x}+ S_{2x}+S_{3x}+S_{4x}$ (where $x$ is the local coordinate), while none of the unperturbed states carry a non-zero value for $M$ as they don't have a magnetic character (all matrix elements are zero ($\langle\psi_i|M|\psi_i\rangle = 0$)). It is possible that the mixing found by perturbation theory will

give rise to a non-zero value of $M$, then the observed magnetic transition can be described using molecular field.

In summary, in the case of two tetrahedra with periodic boundary conditions, we found the mixing in ground state by including the B tetrahedra perturbatively. These states should be investigated to see if they have a magnetic character.

# Chapter 6

# Conclusion and Outlook

**The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.** Paul Dirac

## 6.1 Conclusion

The overall objective of this research was to investigate the frustrated pyrochlore system and find the ground state properties by looking at the symmetry properties of the system which in our case was $Er_2Ti_2O_7$. In order to do so following steps were taken which lead us to the final answer:

1. With the aid of the symmetry properties of the space group $Fd\bar{3}m$, we find the possible states of a single tetrahedron and also the general form of the Heisenberg-Dirac Hamiltonian that governs the system. We have four different exchange coupling constants which determine the ground state. In order to investigate the form of the ground state, we switched two out of four of the interaction off, while keeping other two varying like

periodic functions. The ground state for single tetrahedron was calculated for all six different cases.

2. The ground state for two tetrahedra can be built by direct product of the two ground states. The exchange Hamiltonian for two tetrahedra is $H_A \otimes I + I \otimes H_{A'}$. The direct product preserve the form of the ground state.

3. In $Er_2Ti_2O_7$ we are dealing with a network of tetrahedra. Because of the isolation of single tetrahedron, exact calculation of eigenstates of a single tetrahedron will help us to find the state of the network generally. However, because of the the connectivity of this network, eigenstates of single tetrahedron are not the eigenstate of the entire network. We assumed that there are two types of tetrahedra in pyrochlore lattice, type A and B which were different in overall orientation. A kind of lattice distortion was proposed that lowers the point group symmetry but leaves the crystal system unchanged, was applied to relieve geometrical frustration and arrive to an ordered state. This distortion did not remove the frustration symmetry but led to isolation of individual A type tetrahedra by neglecting exchange interactions on B. By adding the effect of B type terahedra as perturbation, we were able to find the ground state for the system of two tetrahedra more accurately. However, degeneracies of states connected by time reversal symmetry were not lifted by this form of perturbation.

4. The perturbed states can be further used to justify the magnetic characters observed in $Er_2Ti_2O_7$ at low temperatures. By calculating the magnetic order parameter, the states with magnetic properties will have non-zero matrix elements ($\langle\psi_i|M|\psi_i\rangle$)

## 6.2 Outlook

Further analysis can be done by considering 4 tetrahedra and then applying the B type tetrahedra perturbatively. In that case the matrix we are dealing with is a square matrix of dimension 65536 which can be diagonalized numerically for specified values of the coupling constants. In that case, a more vivid picture of the ground state will be constructed which can be used to justify the experimental result of the material that is being studied. By considering 4 tetrahedra, the calculated magnetic order parameter for the ground state will be more precise.

# Postlude

The scientist has a lot of experience with ignorance and doubt and uncertainty, and this experience is of very great importance, I think. When a scientist doesn't know the answer to a problem, he is ignorant. When he has a hunch as to what the result is, he is uncertain. And when he is pretty damn sure of what the result is going to be, he is still in some doubt. We have found it of paramount importance that in order to progress, we must recognize our ignorance and leave room for doubt. Scientific knowledge is a body of statements of varying degrees of certainty  some most unsure, some nearly sure, but none absolutely certain. Now, we scientists are used to this, and we take it for granted that it is perfectly consistent to be unsure, that it is possible to live and not know. But I don't know whether everyone realizes this is true. Our freedom to doubt was born out of a struggle against authority in the early days of science. It was a very deep and strong struggle: permit us to question  to doubt  to not be sure. I think that it is important that we do not forget this struggle and thus perhaps lose what we have gained. **Richard P. Feynman**

# Appendix A

This code was used for in calculations of the 256×256 Hamiltonian. In first set of lines, operators are defined with the aid of Pauli matrices and identity matrix. Then the states in Table (5.1) are defined and the transformation matrix is constructed by direct product of two S matrices. The rest will define the Hamiltonian and diagonalization process of Hamiltonian.

```
J1z = J * KroneckerProduct[PauliMatrix[3], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J2z = J * KroneckerProduct[IdentityMatrix[2], PauliMatrix[3],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J3z = J * KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
     PauliMatrix[3], IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J4z = J * KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], PauliMatrix[3], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J5z = J * KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], PauliMatrix[3],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J6z = J * KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
     PauliMatrix[3], IdentityMatrix[2], IdentityMatrix[2]];
J7z = J * KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], PauliMatrix[3], IdentityMatrix[2]];
J8z = J * KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
     IdentityMatrix[2], IdentityMatrix[2], PauliMatrix[3]];


J1x = KroneckerProduct[PauliMatrix[1], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J2x = KroneckerProduct[IdentityMatrix[2], PauliMatrix[1],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J3x = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    PauliMatrix[1], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J4x = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], PauliMatrix[1], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J5x = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], PauliMatrix[1],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J6x = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    PauliMatrix[1], IdentityMatrix[2], IdentityMatrix[2]];
J7x = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], PauliMatrix[1], IdentityMatrix[2]];
J8x = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], PauliMatrix[1]];
J1y = KroneckerProduct[PauliMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J2y = KroneckerProduct[IdentityMatrix[2], PauliMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J3y = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    PauliMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J4y = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], PauliMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
```

```
J5y = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], PauliMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J6y = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    PauliMatrix[2], IdentityMatrix[2], IdentityMatrix[2]];
J7y = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], PauliMatrix[2], IdentityMatrix[2]];
J8y = KroneckerProduct[IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], IdentityMatrix[2],
    IdentityMatrix[2], IdentityMatrix[2], PauliMatrix[2]];
J1P = T/2 * Table[J1x[[i, j]] + i J1y [[i, j]], {i, 256}, {j, 256}];
J1M = T/2 * Table[J1x[[i, j]] - i J1y [[i, j]], {i, 256}, {j, 256}];
J2P = T/2 * Table[J2x[[i, j]] + i J2y[[i, j]], {i, 256}, {j, 256}];
J2M = T/2 * Table[J2x[[i, j]] - i J2y [[i, j]], {i, 256}, {j, 256}];
J3P = T/2 * Table[J3x[[i, j]] + i J3y [[i, j]], {i, 256}, {j, 256}];
J3M = T/2 * Table[J3x[[i, j]] - i J3y [[i, j]], {i, 256}, {j, 256}];
J4P = T/2 * Table[J4x[[i, j]] + i J4y [[i, j]], {i, 256}, {j, 256}];
J4M = T/2 * Table[J4x[[i, j]] - i J4y [[i, j]], {i, 256}, {j, 256}];
J5P = T/2 * Table[J5x[[i, j]] + i J5y [[i, j]], {i, 256}, {j, 256}];
J5M = T/2 * Table[J5x[[i, j]] - i J5y [[i, j]], {i, 256}, {j, 256}];
J6P = T/2 * Table[J6x[[i, j]] + i J6y[[i, j]], {i, 256}, {j, 256}];
J6M = T/2 * Table[J6x[[i, j]] - i J6y [[i, j]], {i, 256}, {j, 256}];
J7P = T/2 * Table[J7x[[i, j]] + i J7y [[i, j]], {i, 256}, {j, 256}];
J7M = T/2 * Table[J7x[[i, j]] - i J7y [[i, j]], {i, 256}, {j, 256}];
J8P = T/2 * Table[J8x[[i, j]] + i J8y [[i, j]], {i, 256}, {j, 256}];
J8M = T/2 * Table[J8x[[i, j]] - i J8y [[i, j]], {i, 256}, {j, 256}];
S = Table[0, {i, 16}, {j, 16}];
ϵ = -1/2 + I Sqrt[3]/2;
S[[1, 1]] = 1;
S[[2, 8]] = S[[2, 12]] = S[[2, 15]] = S[[2, 14]] = 1/2;
S[[4, 16]] = 1;
```

$$S[[5, 2]] = S[[5, 3]] = S[[5, 5]] = S[[5, 9]] = -\frac{1}{2};$$

$$S[[6, 4]] = S[[6, 13]] = S[[3, 4]] = S[[3, 13]] = \frac{1}{\sqrt{6}};$$

$$S[[6, 6]] = S[[6, 11]] = S[[3, 7]] = S[[3, 10]] = \frac{\epsilon}{\sqrt{6}};$$

$$S[[6, 7]] = S[[6, 10]] = S[[3, 6]] = S[[3, 11]] = \frac{\epsilon^2}{\sqrt{6}};$$

$$S[[7, 9]] = S[[7, 5]] = S[[7, 12]] = S[[7, 8]] = -\frac{1}{\sqrt{8}};$$

$$S[[7, 3]] = S[[7, 2]] = S[[7, 15]] = S[[7, 14]] = \frac{1}{\sqrt{8}};$$

$$S[[8, 8]] = S[[8, 3]] = S[[8, 12]] = S[[8, 2]] = \frac{1}{\sqrt{8}};$$

$$S[[8, 9]] = S[[8, 5]] = S[[8, 14]] = S[[8, 15]] = -\frac{1}{\sqrt{8}};$$

$$S[[9, 13]] = -\frac{1}{\sqrt{2}}; \quad S[[9, 4]] = \frac{1}{\sqrt{2}};$$

$$S[[10, 12]] = S[[10, 14]] = S[[11, 8]] = S[[11, 15]] = \frac{\epsilon^2}{\sqrt{8}};$$

$$S[[11, 12]] = S[[11, 14]] = S[[10, 8]] = S[[10, 15]] = -\frac{\epsilon^2}{\sqrt{8}};$$

$$S[[10, 3]] = S[[10, 5]] = S[[11, 3]] = S[[11, 5]] = \frac{\epsilon}{\sqrt{8}};$$

$$S[[10, 2]] = S[[10, 9]] = S[[11, 2]] = S[[11, 9]] = -\frac{\epsilon}{\sqrt{8}};$$

$$S[[12, 7]] = \frac{1}{\sqrt{2}}; \quad S[[12, 10]] = -\frac{1}{\sqrt{2}};$$

$$S[[14, 2]] = S[[14, 5]] = S[[13, 2]] = S[[13, 5]] = \frac{\epsilon^2}{\sqrt{8}};$$

$$S[[14, 9]] = S[[14, 3]] = S[[13, 9]] = S[[13, 3]] = -\frac{\epsilon^2}{\sqrt{8}};$$

$$S[[13, 14]] = S[[13, 8]] = S[[14, 12]] = S[[14, 15]] = -\frac{\epsilon}{\sqrt{8}};$$

$$S[[13, 12]] = S[[13, 15]] = S[[14, 8]] = S[[14, 14]] = \frac{\epsilon}{\sqrt{8}};$$

$$S[[15, 6]] = \frac{1}{\sqrt{2}}; \quad S[[15, 11]] = -\frac{1}{\sqrt{2}};$$

$$S[[16, 4]] = S[[16, 6]] = S[[16, 7]] = S[[16, 10]] = S[[16, 11]] = S[[16, 13]] = \frac{1}{\sqrt{6}};$$

```
W = Simplify[KroneckerProduct[S, S]];
L = Simplify[ConjugateTranspose[W]];
```

$$X_1 = -\frac{1}{3}\left(J_{1z}\cdot J_{2z} + J_{3z}\cdot J_{4z} + J_{1z}\cdot J_{3z} + J_{2z}\cdot J_{4z} + J_{1z}\cdot J_{4z} + J_{2z}\cdot J_{3z}\right);$$

$$Y_1 = -\frac{1}{3}\left(J_{5z}\cdot J_{6z} + J_{7z}\cdot J_{8z} + J_{5z}\cdot J_{7z} + J_{6z}\cdot J_{8z} + J_{5z}\cdot J_{8z} + J_{6z}\cdot J_{7z}\right);$$

$$Z_1 = -\frac{1}{3}\left(J_{1z}\cdot J_{2z} + J_{7z}\cdot J_{4z} + J_{1z}\cdot J_{7z} + J_{2z}\cdot J_{4z} + J_{1z}\cdot J_{4z} + J_{2z}\cdot J_{7z}\right);$$

$$V_1 = -\frac{1}{3}\left(J_{5z}\cdot J_{6z} + J_{3z}\cdot J_{8z} + J_{5z}\cdot J_{3z} + J_{6z}\cdot J_{8z} + J_{5z}\cdot J_{8z} + J_{6z}\cdot J_{3z}\right);$$

$$\begin{aligned}X_2 = -\frac{\sqrt{2}}{3}\Big(&J_{1z}\cdot(J_{2P}+J_{2M}) + (J_{1P}+J_{1M})\cdot J_{2z} + J_{3z}\cdot(J_{4P}+J_{4M}) + (J_{3P}+J_{3M})\cdot J_{4z} +\\ &J_{1z}\cdot\left(\epsilon J_{3P}+\epsilon^2 J_{3M}\right) + \left(\epsilon J_{1P}+\epsilon^2 J_{1M}\right)\cdot J_{3z} + J_{2z}\cdot\left(\epsilon J_{4P}+\epsilon^2 J_{4M}\right) + \left(\epsilon J_{2P}+\epsilon^2 J_{2M}\right)\cdot J_{4z} +\\ &J_{1z}\cdot\left(\epsilon^2 J_{4P}+\epsilon J_{4M}\right) + \left(\epsilon^2 J_{1P}+\epsilon J_{1M}\right)\cdot J_{4z} + J_{2z}\cdot\left(\epsilon^2 J_{3P}+\epsilon J_{3M}\right) + \left(\epsilon^2 J_{2P}+\epsilon J_{2M}\right)\cdot J_{3z}\Big);\end{aligned}$$

$$\begin{aligned}Y_2 = -\frac{\sqrt{2}}{3}\Big(&J_{5z}\cdot(J_{6P}+J_{6M}) + (J_{5P}+J_{5M})\cdot J_{6z} + J_{7z}\cdot(J_{8P}+J_{8M}) + (J_{7P}+J_{7M})\cdot J_{8z} +\\ &J_{5z}\cdot\left(\epsilon J_{7P}+\epsilon^2 J_{7M}\right) + \left(\epsilon J_{5P}+\epsilon^2 J_{5M}\right)\cdot J_{7z} + J_{6z}\cdot\left(\epsilon J_{8P}+\epsilon^2 J_{8M}\right) + \left(\epsilon J_{6P}+\epsilon^2 J_{6M}\right)\cdot J_{8z} +\\ &J_{5z}\cdot\left(\epsilon^2 J_{8P}+\epsilon J_{8M}\right) + \left(\epsilon^2 J_{5P}+\epsilon J_{5M}\right)\cdot J_{8z} + J_{6z}\cdot\left(\epsilon^2 J_{7P}+\epsilon J_{7M}\right) + \left(\epsilon^2 J_{6P}+\epsilon J_{6M}\right)\cdot J_{7z}\Big);\end{aligned}$$

$$\begin{aligned}Z_2 = -\frac{\sqrt{2}}{3}\Big(&J_{1z}\cdot(J_{2P}+J_{2M}) + (J_{1P}+J_{1M})\cdot J_{2z} + J_{7z}\cdot(J_{4P}+J_{4M}) + (J_{7P}+J_{7M})\cdot J_{4z} +\\ &J_{1z}\cdot\left(\epsilon J_{7P}+\epsilon^2 J_{7M}\right) + \left(\epsilon J_{1P}+\epsilon^2 J_{1M}\right)\cdot J_{7z} + J_{2z}\cdot\left(\epsilon J_{4P}+\epsilon^2 J_{4M}\right) + \left(\epsilon J_{2P}+\epsilon^2 J_{2M}\right)\cdot J_{4z} +\\ &J_{1z}\cdot\left(\epsilon^2 J_{4P}+\epsilon J_{4M}\right) + \left(\epsilon^2 J_{1P}+\epsilon J_{1M}\right)\cdot J_{4z} + J_{2z}\cdot\left(\epsilon^2 J_{7P}+\epsilon J_{7M}\right) + \left(\epsilon^2 J_{2P}+\epsilon J_{2M}\right)\cdot J_{7z}\Big);\end{aligned}$$

$$\begin{aligned}V_2 = -\frac{\sqrt{2}}{3}\Big(&J_{5z}\cdot(J_{6P}+J_{6M}) + (J_{5P}+J_{5M})\cdot J_{6z} + J_{3z}\cdot(J_{8P}+J_{8M}) + (J_{3P}+J_{3M})\cdot J_{8z} +\\ &J_{5z}\cdot\left(\epsilon J_{3P}+\epsilon^2 J_{3M}\right) + \left(\epsilon J_{5P}+\epsilon^2 J_{5M}\right)\cdot J_{3z} + J_{6z}\cdot\left(\epsilon J_{8P}+\epsilon^2 J_{8M}\right) + \left(\epsilon J_{6P}+\epsilon^2 J_{6M}\right)\cdot J_{8z} +\\ &J_{5z}\cdot\left(\epsilon^2 J_{8P}+\epsilon J_{8M}\right) + \left(\epsilon^2 J_{5P}+\epsilon J_{5M}\right)\cdot J_{8z} + J_{6z}\cdot\left(\epsilon^2 J_{3P}+\epsilon J_{3M}\right) + \left(\epsilon^2 J_{6P}+\epsilon J_{6M}\right)\cdot J_{3z}\Big);\end{aligned}$$

$$\begin{aligned}X_3 = \frac{1}{3}\Big(&J_{1P}\cdot J_{2P} + J_{1M}\cdot J_{2M} + J_{3P}\cdot J_{4P} + J_{3M}\cdot J_{4M} + \epsilon^2 J_{1P}\cdot J_{3P} + \epsilon J_{1M}\cdot J_{3M} +\\ &\epsilon^2 J_{2P}\cdot J_{4P} + \epsilon J_{2M}\cdot J_{4M} + \epsilon J_{1P}\cdot J_{4P} + \epsilon^2 J_{1M}\cdot J_{4M} + \epsilon J_{2P}\cdot J_{3P} + \epsilon^2 J_{2M}\cdot J_{3M}\Big);\end{aligned}$$

$$\begin{aligned}Y_3 = \frac{1}{3}\Big(&J_{5P}\cdot J_{6P} + J_{5M}\cdot J_{6M} + J_{7P}\cdot J_{8P} + J_{7M}\cdot J_{8M} + \epsilon^2 J_{5P}\cdot J_{7P} + \epsilon J_{5M}\cdot J_{7M} +\\ &\epsilon^2 J_{6P}\cdot J_{8P} + \epsilon J_{6M}\cdot J_{8M} + \epsilon J_{5P}\cdot J_{8P} + \epsilon^2 J_{5M}\cdot J_{8M} + \epsilon J_{6P}\cdot J_{7P} + \epsilon^2 J_{6M}\cdot J_{7M}\Big);\end{aligned}$$

$$\begin{aligned}Z_3 = \frac{1}{3}\Big(&J_{1P}\cdot J_{2P} + J_{1M}\cdot J_{2M} + J_{7P}\cdot J_{4P} + J_{7M}\cdot J_{4M} + \epsilon^2 J_{1P}\cdot J_{7P} + \epsilon J_{1M}\cdot J_{7M} +\\ &\epsilon^2 J_{2P}\cdot J_{4P} + \epsilon J_{2M}\cdot J_{4M} + \epsilon J_{1P}\cdot J_{4P} + \epsilon^2 J_{1M}\cdot J_{4M} + \epsilon J_{2P}\cdot J_{7P} + \epsilon^2 J_{2M}\cdot J_{7M}\Big);\end{aligned}$$

$$\begin{aligned}V_3 = \frac{1}{3}\Big(&J_{5P}\cdot J_{6P} + J_{5M}\cdot J_{6M} + J_{3P}\cdot J_{8P} + J_{3M}\cdot J_{8M} + \epsilon^2 J_{5P}\cdot J_{3P} + \epsilon J_{5M}\cdot J_{3M} +\\ &\epsilon^2 J_{6P}\cdot J_{8P} + \epsilon J_{6M}\cdot J_{8M} + \epsilon J_{5P}\cdot J_{8P} + \epsilon^2 J_{5M}\cdot J_{8M} + \epsilon J_{6P}\cdot J_{3P} + \epsilon^2 J_{6M}\cdot J_{3M}\Big);\end{aligned}$$

$$X_4 = -\frac{1}{6}\,(J_{1P}.J_{2M} + J_{1M}.J_{2P} + J_{3P}.J_{4M} + J_{3M}.J_{4P} + J_{1P}.J_{3M} + J_{1M}.J_{3P} + J_{2P}.J_{4M} + J_{2M}.J_{4P} + J_{1P}.J_{4M} + J_{1M}.J_{4P} + J_{2P}.J_{3M} + J_{2M}.J_{3P});$$

$$Y_4 = -\frac{1}{6}\,(J_{5P}.J_{6M} + J_{5M}.J_{6P} + J_{7P}.J_{8M} + J_{7M}.J_{8P} + J_{5P}.J_{7M} + J_{5M}.J_{7P} + J_{6P}.J_{8M} + J_{6M}.J_{8P} + J_{5P}.J_{8M} + J_{5M}.J_{8P} + J_{6P}.J_{7M} + J_{6M}.J_{7P});$$

$$Z_4 = -\frac{1}{6}\,(J_{1P}.J_{2M} + J_{1M}.J_{2P} + J_{7P}.J_{4M} + J_{7M}.J_{4P} + J_{1P}.J_{7M} + J_{1M}.J_{7P} + J_{2P}.J_{4M} + J_{2M}.J_{4P} + J_{1P}.J_{4M} + J_{1M}.J_{4P} + J_{2P}.J_{7M} + J_{2M}.J_{7P});$$

$$V_4 = -\frac{1}{6}\,(J_{5P}.J_{6M} + J_{5M}.J_{6P} + J_{3P}.J_{8M} + J_{3M}.J_{8P} + J_{5P}.J_{3M} + J_{5M}.J_{3P} + J_{6P}.J_{8M} + J_{6M}.J_{8P} + J_{5P}.J_{8M} + J_{5M}.J_{8P} + J_{6P}.J_{3M} + J_{6M}.J_{3P});$$

```
HA = (C1 (X1) + C2 (X2) + C3 (X3) + C4 (X4));
HB = (C1 (Y1) + C2 (Y2) + C3 (Y3) + C4 (Y4));
HP = C5 (Z1 + V1) + C6 (Z2 + V2) + C7 (Z3 + V3) + C8 (Z4 + V4);
HT = HA + HB + HP;
Simplify[HT];
MatrixForm[HT];

F = W. HT;
G = Simplify[F];
Q = G.L;

QQ = Simplify[Q];
MatrixForm[QQ]


Eigenvalues[QQ]

(*MatrixForm[AA1= Table[QQ[[i,j]],{i,17,30},{j,256,256}]]
  MatrixForm[AA2= Table[BB[[i,j]],{i,17,30},{j,256,256}]]
  HT.L[[256]]
  MatrixForm[AA2= Table[BB[[i,j]],{i,160,170},{j,256,256}]]
  X11=Table[L[[i,256]], {i,256}]
  MatrixForm[HT.X11]*)
```

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[25] Mathematica software from Wolfram licensed by Memorial University was used.

[26] Unpublished work by A. Bertin, Y. Chapuis, P. Dalmas de Reotier and A.Yaouane